PB86-118197

# Volatile Organic Chemicals
# Methods and Monitoring
# Document (Draft)

(U.S.) Environmental Protection Agency
Washington, DC

Jun 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-118197

# VOLATILE ORGANIC CHEMICALS: METHODS AND MONITORING DOCUMENT

June 1985

DRAFT

Criteria and Standards Division
Washington, D.C.

and

Technical Support Division
Cincinnati, Ohio
Office of Drinking Water
U.S. Environmental Protection Agency

16

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

## TECHNICAL REPORT DATA

*(Please read Instructions on the reverse before completing)*

**2.**

**3. RECIPIENT'S ACCESSION NO.**
PB86 118197/AS

**SUBTITLE**
Volatile Organic Chemicals: Methods and
Monitoring Document

**5. REPORT DATE**
6/85

**6. PERFORMING ORGANIZATION CODE**

**HOR(S)**
U.S. Environmental Protection Agency

**8. PERFORMING ORGANIZATION REPORT NO.**

**PERFORMING ORGANIZATION NAME AND ADDRESS**
Same as box 12.

**10. PROGRAM ELEMENT NO.**

**11. CONTRACT/GRANT NO.**

**12. SPONSORING AGENCY NAME AND ADDRESS**
U.S. Environmental Protection Agency
Office of Drinking Water (WH-550)
401 M St., S.W., Washington, D.C. 20460

**13. TYPE OF REPORT AND PERIOD COVERED**
Scientific report

**14. SPONSORING AGENCY CODE**
EPA/CSD

**15. SUPPLEMENTARY NOTES**

**16. ABSTRACT**

The Office of Drinking Water (ODW) and Technical Support Divison (TSD), U.S. Environmental Protection Agency have prepared a methods and monitoring document for volatile organic chemicals in drinking water. The purpose of this document is to produce information which will serve as a basis for the development of compliance monitoring requirements for the volatile organic chemicals in EPA's Maximum Contaminant Level (MCL) proposal. This document discusses the following topics:

- Whether the analytical methods available are economically and technologically feasible to determine compliance with the MCLs.
- A variety of sample collection issues upon which compliance monitoring requirements can be based.
- An evaluation of the available occurrence data to determine whether the vulnerability of drinking water sources to contamination by VOCs may be predicted.
- The proposed compliance monitoring requirements and the projected costs associated with these requirements.

**17. KEY WORDS AND DOCUMENT ANALYSIS**

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Analytical methods<br>Volatile organic chemicals<br>Monitoring<br>Drinking Water | | |

| | | |
|---|---|---|
| **18. DISTRIBUTION STATEMENT**<br>OPEN | **19. SECURITY CLASS** *(This Report)*<br>Non-sensitive | **21. NO. OF PAGES**<br>124 |
| | **20. SECURITY CLASS** *(This page)*<br>Non-sensitive | **22. PRICE** |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

VOC Methods and Monitoring Document

## Table of Contents

Page

Glossary ........................................ ii

I. Introduction ................................... 1

II. Compliance Monitoring Requirements ................. 6

III. Determination of Compliance with MCL .............. 17

IV. Analytical Methods ............................. 20

V. Monitoring Considerations ....................... 45

VI. Monitoring for Unregulated VOCs ................... 59

VII. Monitoring Costs ............................... 71

References ...................................... 74

Appendix A ......................................A-1

Appendix B ......................................B-1

# GLOSSARY

| Term | Definition |
|---|---|
| CMR | Compliance Monitoring Requirements |
| CWA | Clean Water Act |
| CWS | Community Water System(s) |
| CWSS | Community Water Supply Survey |
| DS | Distribution System(s) |
| DW | Drinking Water |
| EPA | United States Environmental Protection Agency |
| FRDS | Federal Reporting Data System |
| FWPCA | Federal Water Pollution Control Act |
| GC | Gas Chromatograph(ic) |
| GW | Ground Water |
| GWS | Ground Water System(s) |
| GWSS | EPA Ground Water Supply Survey |
| MCL | Maximum Contaminant Level |
| MW | Molecular Weight |
| NOMS | National Organics Monitoring Survey |
| NORS | National Organics Reconnaissance Survey for halogenated organics |
| NPDES | National Pollutant Discharge Elimination System |
| NSP | National Screening Program for organics in drinking water |
| ODW | Office of Drinking Water of EPA |
| pop. | Population |
| primacy authority | Refers to the entity that possesses primary enforcement authority under the SDWA. |
| QL | Quantitation Limit, which is generally defined by instrumental and other analytical factors, is the lowest, reliable measure of concentration. |
| RCRA | Resource Conservation and Recovery Act |
| Rev. Reg. | Revised Regulations - Phase I |
| RMCL | Recommended Maximum Contaminant Level |
| RWS | Rural Water Survey |
| Sanitary Survey | See "Watershed Analysis" |
| SDWA | Safe Drinking Water Act of 1974 |
| SW | Surface Water |
| SWS | Surface Water System(s) |
| THMs | 4 Trihalomethanes Regulated in 44 (231) CFR 68624 (1979) |
| TSCA | Toxic Substances Control Act |
| TSD | Technical Support Division of ODW |
| USGS | U.S. Geological Survey |
| VOCs | Volatile Organic Chemicals: low MW and relatively water-insoluble hydrocarbons and halocarbons measured by EPA Methods 502.1, 503.1 and 524.1 |
| 9 VOCs | 9 VOCs listed in VOC RMCL, Fed. Reg. 49 (114), 24430 |
| Watershed Analysis | A _nom_ _de_ _plume_ for the well-known term "sanitary survey" |
| WTP | Water Treatment Plant |

# GLOSSARY

| Term | Definition |
|---|---|
| CMR | Compliance Monitoring Requirements |
| CWA | Clean Water Act |
| CWS | Community Water System(s) |
| CWSS | Community Water Supply Survey |
| DS | Distribution System(s) |
| DW | Drinking Water |
| EPA | United States Environmental Protection Agency |
| FRDS | Federal Reporting Data System |
| FWPCA | Federal Water Pollution Control Act |
| GC | Gas Chromatograph(ic) |
| GW | Ground Water |
| GWS | Ground Water System(s) |
| GWSS | EPA Ground Water Supply Survey |
| MCL | Maximum Contaminant Level |
| MW | Molecular Weight |
| NOMS | National Organics Monitoring Survey |
| NORS | National Organics Reconnaissance Survey for halogenated organics |
| NPDES | National Pollutant Discharge Elimination System |
| NSP | National Screening Program for organics in drinking water |
| ODW | Office of Drinking Water of EPA |
| pop. | Population |
| primacy authority | Refers to the entity that possesses primary enforcement authority under the SDWA. |
| QL | Quantitation Limit, which is generally defined by instrumental and other analytical factors, is the lowest, reliable measure of concentration. |
| RCRA | Resource Conservation and Recovery Act |
| Rev. Reg. | Revised Regulations - Phase I |
| RMCL | Recommended Maximum Contaminant Level |
| RWS | Rural Water Survey |
| Sanitary Survey | See "Watershed Analysis" |
| SDWA | Safe Drinking Water Act of 1974 |
| SW | Surface Water |
| SWS | Surface Water System(s) |
| THMs | 4 Trihalomethanes Regulated in 44 (231) CFR 68624 (1979) |
| TSCA | Toxic Substances Control Act |
| TSD | Technical Support Division of ODW |
| USGS | U.S. Geological Survey |
| VOCs | Volatile Organic Chemicals:  low MW and relatively water-insoluble hydrocarbons and halocarbons measured by EPA Methods 502.1, 503.1 and 524.1 |
| 9 VOCs | 9 VOCs listed in VOC RMCL, Fed. Reg. 49 (114), 24430 |
| Watershed Analysis | A nom de plume for the well-known term "sanitary survey" |
| WTP | Water Treatment Plant |

# I. INTRODUCTION

The U. S. Environmental Protection Agency (EPA) has proposed regulations for certain VOCs that have been detected in finished drinking waters. The VOCs are man-made chemicals consisting of low molecular weight aliphatic and aromatic hydrocarbons, many of which are halogenated. These contaminants are most commonly found in large population areas where industrial and other human activities are prevalent. EPA's Office of Drinking Water (ODW) is developing primary drinking water regulations for the nine VOCs listed below:

Trichloroethylene
Tetrachloroethylene
Carbon tetrachloride
1,1,1-Trichloroethane
1,2-Dichloroethane
Vinyl Chloride
Benzene
p-Dichlorobenzene
1,1-Dichloroethylene

This chapter presents some brief background information on VOC contamination of drinking water supplies, the purposes of this document and outlines the content of the chapters that follow.

## Background

EPA has conducted five major national surveys since 1975 that provide data on the occurrence of VOCs in drinking water. These are:

National Organics Reconnaissance Survey for Halogenated Organics (NORS)
National Organics Monitoring Survey (NOMS)
National Screening Program for Organics in Drinking Water (NSP)
Community Water Supply Survey (CWSS)
Ground Water Supply Survey (GWSS)

These Federal surveys and other State data indicate that VOCs occur in both surface and ground waters. Most systems sampled in the first three national surveys listed above were surface water supplies. Several volatile organics (besides the trihalomethanes) were found frequently in the few ground waters sampled. This finding and results from State and local monitoring efforts prompted the two more recent studies which focused on ground water contamination. These studies confirmed that several volatile organic chemicals, such as trichloroethylene and tetrachloroethylene, occur frequently in systems using ground water sources. This recent information contradicts the belief held for many years that ground waters are naturally protected from contamination by human activities. The problem in ground waters is potentially more severe than in surface waters because, once contaminated, ground waters may remain that way for a long time.

The sources of contamination of drinking water supplies by VOCs are various. Traditionally, surface waters have been considered more susceptible to contamination because of the discharge of municipal and industrial wastes to surface waters. Occasional spills have also contributed to severe temporary contamination of surface waters. It is now recognized that infiltration of organic chemicals into ground water is occurring and that it is largely due to the disposal of municipal and industrial wastewater and solid wastes on the land. This is particularly a problem in those instances where a landfill is located over permeable soil above a shallow water table. Ground water contamination also may occur as a result of accidental spills and underground leaking storage tasks.

Surface water contamination incidents due to known discharges or spills are usually short term and easy to monitor. For ground waters, however, contamination is more difficult to predict or characterize since infiltration of contaminants into ground water is a slow process, governed by many complex and often poorly defined factors.

The Safe Drinking Water Act (SDWA) (42 USC 300f, *et seq*.) requires EPA to assure that public water systems provide safe drinking water. The SDWA under Sections 1401 and 1412 requires EPA to establish primary drinking water regulations which 1) apply to public water systems; 2) specify contaminants which in the judgement of the Administrator, may have any adverse effect upon the health of persons; and 3) specify for each contaminant either a maximum contaminant level (MCL) or a treatment technique. An MCL will be established for a contaminant if it is economically and technologically feasible to ascertain the level of such contaminant in water. Also, section 1445 of the SDWA provides the Administrator with a broad authority to require monitoring of drinking water supplies for unregulated contaminants.

Recommended maximum contaminant levels (RMCLs) were proposed in the June 12, 1984 *Federal Register* for the nine VOCs listed above. The Agency will finalize the RMCLs for the nine VOCs and simultaneously propose MCLs for these contaminants shortly. This action will be followed by promulgation of MCLs including monitoring and reporting requirements.

ODW is also considering the development of monitoring regulations for the nine VOCs in the RMCL proposal and additional VOCs in drinking water supplies under the authority of section 1445 of the SDWA. The primary goal of a monitoring regulation will be to accelerate monitoring for contaminants to be included in the revised regulations and to detect cases of contamination for other unregulated VOCs.

## Purpose

The purpose of this document is to provide information which will serve as a basis for the development of compliance monitoring requirements (CMR) for nine VOCs in the MCL proposal. The major technical efforts associated with this task include the following:

- determine whether the analytical methods available are economically and technologically feasible to determine compliance with the MCLs.
- examine pertinent sample collection issues upon which compliance monitoring requirements can be based.
- evaluate available occurrence data to determine whether the vulnerability of drinking water sources to contamination by VOCs may be predicted.
- present proposed compliance monitoring requirements and the projected costs associated with these requirements.

## Contents

The contents of chapters that follow is summarized below:

Chapter II presents proposed compliance monitoring requirements for the VOCs which includes the phasing of systems into compliance over a four year period by population size. All systems will be required to monitor. The proposed scheme provides for a minimum resampling frequency based on initial monitoring results and other vulnerability ranking criteria.

Chapter III presents information on the determination of compliance with the MCLs for these contaminants.

Chapter IV presents an evaluation of the analytical methods available for the determination of VOCs in drinking water supplies. This chapter also presents information useful in the development of performance criteria for those laboratories analyzing compliance samples.

Chapter V presents a discussion of the collection of samples representative of VOC concentrations reaching the consumer. The collection of representative samples includes a discussion of the following issues:

- where to sample (source, at the point(s) when the water enters the distribution system, or the consumer's faucet)
- how many samples (number of samples per system)
- when to sample (sampling period).

It also discusses criteria useful in predicting the vulnerability of systems to VOC contamination, providing a basis for ranking systems to establish monitoring priorities and resampling frequency.

Chapter VI provides a discussion of possible monitoring regulations for the nine VOCs and other unregulated VOCs.

Chapter VII provides a summary of projected monitoring costs for compliance and for unregulated VOCs.

## II. COMPLIANCE MONITORING REQUIREMENTS

This chapter provides proposed minimum national monitoring requirements for the nine VOCs. The complexities of taking representative samples within individual systems and the potential for variability of water quality with time in surface and ground water systems have been taken into account in developing this sampling scheme. Setting monitoring requirements encompasses many issues such as the number of samples, frequency of sampling, location of sampling points, which systems should sample and when the sampling should be done. Fundamental to the approach taken in setting monitoring requirements are the following assumptions:

(1) Different requirements would be set for ground water versus surface water systems.

The characteristics and mechanisms of contamination of ground and surface water sources are such that different monitoring requirements should be developed for each type of system. Generally, contamination of SW is more variable over short time periods while GW tend to stay contaminated longer.

(2) All systems should conduct at least one round of monitoring.

State and federal data indicate that some states have had only limited success in identifying sites contaminated with one or more of the VOCs. That is, VOC contamination is not always predictable based upon VOC occurrence trends. It follows that all systems should conduct at least an initial round of monitoring to determine compliance because one can not reliably predict what systems have VOC contamination. This approach would afford maximum consumer protection.

(3) Phasing of monitoring requirements is needed. Phasing-in the monitoring requirements is a prudent way to provide systems and states enough time to allocate the necessary resources for this program. Resources are limited in state programs and immediate monitoring for VOCs could impose a heavy financial burden on many small systems. In addition, phasing-in the monitoring requirements will allow the analytical laboratories to expand their capability to handle additional samples. Expansion of the laboratory capabilities includes the acquisition of all the necessary equipment and the training of laboratory personnel to conduct VOCs analyses. Laboratories presently analyzing trihalomethanes by purge-and-trap gas chromatography (GC) may have to invest in a photoionization detection or mass spectrometer system. Those laboratories presently analyzing trihalomethanes by liquid-liquid extraction GC may have to invest in purge-and-trap GC equipment with an appropriate detection system.

(4) Minimum requirements for repeat sampling are needed. Traditionally surface waters have been considered

> more susceptible than ground waters to contamination by VOCs and other organic chemicals because of the discharge of municipal and industrial wastes to surface waters. However, recent surveys have shown that ground waters are also being contaminated by a variety of organic compounds. Both ground and surface water systems can become vulnerable to contamination with changing land use and waste disposal practices. Thus, a minimum requirement for repeat sampling is needed to determine possible changes in water quality with time.

The rationale for this approach is more explicitly given in following chapters and Appendix A.

## Monitoring Alternatives

Compliance monitoring requirements may range from an extensive federal monitoring program to a monitoring program largely implementable at the discretion of the States. Three possible monitoring options are summarized at the end of this chapter. The three options are more explicitly discussed in Appendix B. The middle option is recommended as the most appropriate since it provides certain minimum federal requirements with provisions for State discretion in their implementation. A more detailed discussion of the proposed monitoring requirements is provided below.

## Proposed Minimum Federal Requirements

### Implementation Schedule

All CWS will monitor once during the initial monitoring period. The monitoring program will be phased-in over four years based on the size of the population served by the CWS. Monitoring is to be completed according to the following schedule based on the date of promulgation of these regulations:

1. Systems serving over 10,000 are to complete the initial monitoring within one year of the date of the rule;
2. Systems serving from 3,300 to 10,000 are to complete the initial monitoring within two years of the date of the rule; and
3. Systems serving under 3,300 are to complete the initial monitoring within four years of the date of the rule.

The schedule for the initial round of monitoring is based solely on system size under the assumptions that many larger systems are more vulnerable to VOC contamination and that they can best afford the financial expense associated with the monitoring requirements. The States should use discretion in prioritizing which systems ought to monitor first within a given system size based on suspected vulnerability of a system. The States will be encouraged to assess the vulnerability of CWS to VOC contamination and to accelerate monitoring for the most vulnerable systems. General criteria for ranking system vulnerability are included in Chapter V.

## Sampling for Ground Water Systems

The first round of monitoring includes a minimum of one sample at each entry point to the distribution system (quarterly sampling is preferable for one year if VOCs are detected in the first sample). The number of samples may be reduced if the system can demonstrate that multiple wells have essentially the same water quality under different combinations of pumping volume and duration that are used by the system. Some systems have on-going monitoring programs which provide data on water source quality. Such data can be used by the states to determine if either a reduction or an increase in the number of sampling points is warranted.

The minimum requirement for repeat monitoring is based on the vulnerability of systems instead of system size. Those systems judged to be vulnerable because of initial monitoring results or by other criteria such as those discussed in chapter V will monitor more frequently than systems determined not to be vulnerable. The minimum frequency of repeat monitoring is as follows:

| Concentration of any VOC | Frequency |
|---|---|
| not detected, not vulnerable | 5 years |
| not detected, vulnerable | 3 years |
| detected | quarterly |

For "not-vulnerable" systems, the minimum frequency of repeat monitoring will be every five years. However, the system must notify the state of any changes (e.g., change in water source) which may result in a reclassification of the system from not-vulnerable to vulnerable. The state must recertify the system's vulnerability status every year.

## Sampling for Surface Water Systems

The first round of monitoring includes one sample per each treatment plant or source used by the system at the tap, once per quarter for one year. VOCs monitoring could be tied into the THMs monitoring for some systems serving a population of 10,000 and above. Large systems on surface waters that are vulnerable are encouraged to monitor monthly.

The minimum requirement for repeat monitoring for surface water systems is also based on the vulnerability of the system and on whether VOCs have been previously detected. It includes one sample per each treatment plant or source used by the system, quarterly during the monitoring period. Samples should be taken during the most vulnerable times (e.g. times of discharges, spills).

The minimum frequency of repeat monitoring is as follows:

| Concentration of any VOC | Frequency |
|---|---|
| not detected, not vulnerable | State discretion |
| not detected, vulnerable | 3 years |
| detected | quarterly |

For "not-vulnerable" systems, the minimum frequency of repeat monitoring will be up to the discretion of the State. However, the state must recertify the system's vulnerability status annually by a watershed analysis. When VOCs are detected in a "not-vulnerable" system, that system is automatically reclassified to be vulnerable.

## Mixed Ground Water and Surface Water Systems

For those systems utilizing both ground and surface waters, the monitoring requirements described above apply per type of source.

## SUMMARY OF PROPOSED MONITORING OPTION

The goal of a national monitoring program is to provide a sampling scheme that efficiently uses time, money and personnel while providing a good indication of consumer exposure to contaminants in drinking water. Every system will conduct an initial round of monitoring phased-in over 4 years. For both ground and surface water systems, the proposed monitoring requirements give the smaller communities a longer period of time to comply with the regulations as a practical matter since their resources are generally more limited than for larger systems. Also, many larger systems are generally more vulnerable to VOC contamination than smaller systems due to their proximity to industrial activity. Thus priorities for the initial monitoring period have been based on population being served by the system. Other considerations affecting vulnerability (see chapter V) should be used by the States to prioritize the monitoring of systems within a given size category.

The minimum requirements for repeat monitoring are not based on the size of the system but on whether or not VOCs were found in previous monitoring or whether or not the system is considered vulnerable. The monitoring frequency includes sampling each quarter for surface water systems and sampling at least once for ground water systems since variability of surface water quality is expected to be influenced more by seasonal and weather conditions. However, those ground water systems which detect VOCs in the initial sample should sample during four consecutive quarters to obtain an average concentration for the determination of compliance.

A "not-vulnerable" system can change to a vulnerable status when one or more of the conditions affecting vulnerability change. Therefore, the frequency of repeat monitoring should not be based exclusively on the results from the previous monitoring round but also on a watershed analysis. The State is responsible for certifying the vulnerability status of the system on a yearly basis. The guidelines for determining vulnerability discussed in chapter V may be used for this purpose, or the state may develop more specific criteria using these guidelines. The system must notify the state if there is any change that could affect the vulnerability of the system such as use of a new water source.

## SUMMARY OF OPTION 1

### Initial Monitoring

- All systems monitor once over 4 years
- Phase in by size:

| | |
|---|---|
| >10,000 | complete by end of 1 year |
| 3,300-10,000 | complete by end of 2 years |
| <3,300 | complete by end of 4 years |

- Ground Water Systems:
  - Sample locations: sample at each entry point to the distribution system.
  - Number of samples: quarterly sampling for one year (i.e., 4 samples). Require resample of any positive result.
- Surface Water Systems:
  - Sample locations: sample in distribution system at points representative of each source.
  - Number of samples: one sample per source or treatment plant, quarterly for one year, require resample of any positive result.

### Repeat Monitoring

All systems would be required to monitor for the nine VOCs on a frequency based upon the results of the first monitoring and their vulnerability to VOC contamination.

| **Status*** | **Frequency** |
|---|---|
| VOCs not detected and not vulnerable | Repeat in 5 years |
| VOCs not detected and vulnerable | Repeat in 3 years |
| VOCs detected | Monthly |

* States would recertify annually vulnerability status.

## SUMMARY OF OPTION 2

### Initial Monitoring

- All systems monitor once over 4 years
- Phase in by size:

| | |
|---|---|
| >10,000 | complete by end of 1 year |
| 3,300-10,000 | complete by end of 2 years |
| <3,300 | complete by end of 4 years |

- Ground Water Systems:
  - Sample locations: sample at each entry point to the distribution system.
  - Number of samples: one sample (or quarterly sample for one year if initial sample is positive); State discretion on confirmation sample.
- Surface Water Systems:
  - Sample locations: sample in distribution system at points representative of each source.
  - Number of samples: one sample per source or treatment plant quarterly for one year; State discretion on confirmation samples.

### Repeat Monitoring

Repeat compliance monitoring would be based upon vulnerability and if VOCs were detected, similar to Option 1.

| • Status* | Frequency | |
|---|---|---|
| | Ground Water | Surface Water |
| VOCs not detected, not vulnerable | Repeat in 5 years | State discretion |
| VOCs not detected and vulnerable | Repeat in 3 years | Repeat in 3 years |
| VOCs detected | Quarterly | Quarterly |

* States would recertify annually vulnerability status.

## SUMMARY OF OPTION 3

### Initial Monitoring

- All systems monitor once over 5 years
- Phase in by size:

| | |
|---|---|
| >10,000 | complete by end of 1 year |
| 3,300-10,000 | complete by end of 2 years |
| 500-3,300 | complete by end of 4 years |
| <500 | complete by end of 5 years |

- Ground Water Systems:
  - Sample locations: sample at entry points to the distribution system.
  - Number of samples: minimum of one sample (at least 25% of entry points must be sampled); State discretion on confirmation sample.
- Surface Water Systems: State discretion based upon vulnerability assessment.

### Repeat Monitoring

Repeat compliance monitoring would only be for those systems that detected VOCs in the first round. Other systems would be at State discretion.

| Status* | Frequency |
|---|---|
| VOCs not detected and not vulnerable | State discretion |
| VOCs not detected and vulnerable | State discretion |
| VOCs detected | Annually |

* States would recertify annually vulnerability status.

## III. DETERMINATION OF COMPLIANCE WITH MCL

The sampling locations for GWS are at the entry points to the distribution system. GWS will be monitored at least once at each sampling point during the initial sampling period. However, if the initial sample is positive, the number of samples is increased immediately to one sample per quarter for one year. The sampling locations for SWS are in the distribution system at points representative of the water delivered by each treatment plant or source. SWS will be monitored quarterly for one year during the initial monitoring period.

Two possible approaches for determination of compliance are (1) averaging the results of all sampling locations within the system or (2) determining compliance in individual portions of the system. For purposes of reporting to the primary agency, averaging the results is most practical. However, in systems with multiple wells or treatment plants some consumers may be exposed continuously to high levels of VOCs since the contamination may be confined to a portion of the system. Determination of compliance by averaging the results from various sampling points could mask the high exposure of these consumers. In the interest of providing protection to all consumers, the following procedure is recommended to determine compliance with the MCL:

1. Averaging the individual results will be allowed for reporting purposes when VOC concentrations are below the MCL at all sampling points within the system.

2. In cases where results from one or more sampling locations exceed the MCL for any VOC, an average result may be reported to the primary agency, but systems will also be required to report individual results for those locations exceeding the MCL and to notify the affected consumers.

3. A system is out of compliance if any portion of the system has average VOC levels above the MCL.

4. Repeat monitoring requirements apply separately to each treatment plant or source in the system. For example, only those portions of a system where VOCs are detected will be required to monitor quarterly. Compliance for that portion of the system will be determined by averaging the quarterly values of the preceding twelve months. For calculating the running annual average, equal weight will be given to the quarterly samples.

5. For SWS, the monitoring requirements specify quarterly sampling during the monitoring period. Compliance with the MCL will be determined by averaging the preceding four quarters.

   If successive monitoring indicates that VOC levels have decreased below detection (due to such factors as fluctuations in source water quality, change in water source or treatment) and a satisfactory record of at least three years shows that the VOC levels in every four consecutive quarters stay consistently below detection, a system may request a reduction in the monitoring frequency and elimination of the public notification requirement. The reporting of compliance results should be done to the same number of significant figures as the MCL. Rounding-off numbers should be made in accordance with Water Supply Guidance No. 72. If the resulting average is greater than the MCL, the system is out of compliance.

## IV. ANALYTICAL METHODS

The analytical methods available for the determination of VOCs in finished drinking water samples are assessed in this chapter. Performance characteristics of each analytical method will be used in making the following regulatory decisions:

- specifying analytical methods for the determination of compliance with the regulations, and
- development of acceptance criteria to evaluate the performance of laboratories analyzing compliance samples.

### BACKGROUND

Section 1401 of the SDWA requires that an MCL be set for a specific contaminant which in the judgement of the Administrator may have an adverse effect on the health of persons if "it is economically and technologically feasible to ascertain the level of such contaminant in water in public water systems." If monitoring is not feasible, a treatment technique requirement is specified. The determination of feasibility of the sampling and analytical methodology used to determine compliance with MCLs requires the consideration of a number of factors, including: sampling techniques and sample preparation including volume of sample, preservation, transport and holding times; precision and accuracy; detection limits; laboratory availability/capabilities; laboratory experience with the method (widespread versus limited use); extent of method validation (reliability); and cost of analysis (cost per sample and monitoring costs).

These factors are addressed for the different analytical methods available with emphasis on the determination of the nine VOCs that have been proposed for regulation.

Section 1401 of the SDWA also defines a primary drinking water regulation in part as consisting of ". . . criteria and procedures to assure a supply of drinking water which dependably complies with such maximum contaminant levels; including quality control and testing procedures to insure compliance . . ." In addition, the regulations at 40 CFR 141.28 require that all testing done for compliance purposes be performed by laboratories approved by either the EPA or those States with primary enforcement responsibility. Therefore, this chapter will also address performance criteria for those laboratories analyzing compliance samples and laboratory certification.

## STATE-OF-THE-ART

The existing analytical methods for VOCs and development of improved procedures for these contaminants are current concerns. The most important requirements of methods of analysis used for compliance monitoring are accuracy (lack of bias) and precision (good reproducibility) at least at or near the maximum contamination level (MCL). The selected methods should also be sufficiently specific to meet the data needs in the presence of interfering substances. These characteristics must be balanced against practical considerations of cost, time and level of training required (1). The selection of analytical methods for compliance with VOC regulations has taken into account all these factors.

Numerous methods have been developed for the determination of volatile organic chemicals in drinking water. These methods involve the use of gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). The EPA methods are: "Method 502.1 Volatile Halogenated Organic Compounds in Water by Purge and Trap Gas Chromatography," "Method 503.1 Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography," and "Method 524.1 Volatile Organic Compounds in Water by Purge and Trap Gas Chromatography/Mass Spectrometry." In these methods (2-4), the purge and trap technique is used to extract and concentrate compounds which exhibit low water solubilities and vapor pressures greater than water. This is followed by separation in a GC column, detection and quantitation with a conventional detector or a mass spectrometer.

Below is a discussion of the sampling procedures followed by a description of the applicability and capabilities of available analytical methods. The performance data in the written analytical methods include single- and multilaboratory data.

## Sampling Procedures

Sample bottles must be cleaned and filled according to the procedures described in the methods. Duplicate field reagent blanks must accompany each set of sample bottles to the sampling sites and back to the laboratory. All samples should be collected in duplicate.

The samples must be preserved with hydrochloric acid to a pH<2 and then chilled to 4°C from the time of collection until analysis. The analysis must be completed within 14 days of sample collection. EMSL-CI is conducting studies to provide additional analytical data related to the recommended sample preservation technique and holding times for analysis of VOCs. The sample preservation and storage requirements may be modified in the future as a result of these on-going studies.

## Description of Available Methods

### Method 502.1

Summary - An inert gas is bubbled through a 5 mL. water sample contained in a specially designed purging device. Volatile constituents are transferred from the aqueous phase to the gaseous phase. The compounds are swept from the purging device and are trapped in a short column containing a sorbent material. The trapped compounds are then thermally desorbed and backflushed onto the head of a packed GC column. The GC is temperature programmed to separate the halogenated compounds that are detected with a halide specific detector.

Applicability - This method can be used to measure the VOCs of concern except for benzene. Benzene and other non-halogenated VOCs are not measured with the detection system employed in this method.

Method Performance - Data included in this method were obtained with a Hall model 700A electrolytic conductivity detector. Quantitation limits are estimated at approximately

0.5 ug/L for most compounds (6). Single laboratory accuracy and precision data for concentrations below 1 ug/L are summarized in the method for many halogenated VOCs including those of concern in drinking water. Accuracy, expressed as mean recoveries, range from 88 to 110% for the VOCs in the RMCL proposal. Precision, expressed as relative standard deviations, range from 6.0 to 15% for these VOCs.

Method 503.1

Summary - The purge and trap extraction/concentration technique previously described is also used for volatile aromatic compounds. The GC is temperature programmed to separate the aromatic compounds that are detected with a photoionization detector.

Applicability - This method can be used to measure benzene, p-dichlorobenzene and other volatile aromatics and unsaturated compounds such as trichloroethylene.

Method Performance - Quantitation limits are estimated at approximately 0.5 ug/L for most aromatics (6). Single laboratory precision and accuracy data for concentrations below 1 ug/L are summarized in the method for about 30 compounds. Mean recovery was 100% and relative standard deviation was 2.8% for benzene. Mean recovery was 95% and relative standard deviation was 6.4% for p-dichlorobenzene.

Method 524.1

Summary - The purge and trap technique previously described is used to extract and concentrate a 25 mL. aqueous sample. Components are separated by GC and are tentatively identified by their mass spectra. Tentative identifications are confirmed by analyzing standards under the same conditions used for the samples.

Applicability - This method can be used to determine a wide range of volatile organic compounds. Benzene and other aromatics are analyzed along with many halogenated VOCs. The method covers the determination of all the VOCs included in the RMCL proposal.

Method Performance - Method detection limits (MDLs) and quantitation limits for this method are comparable to those obtained with Methods 502.1 and 503.1. Single laboratory precision and accuracy have been determined for the nine VOCs by analysis of seven aliquats of reagent water spiked at levels of 1.0 or 5.0 ug/L. The results show average recoveries ranging from 88 to 109% and relative standard deviations ranging from 3.6 to 13.6%.

## Detection Limits

A recent survey (5) of seven U.S. EPA laboratories and contract laboratories serving the EPA, disclosed approximate detection limits averaging from 0.2 to 0.5 ug/L for the nine VOCs in the proposed regulation. Table 1 summarizes the results of this survey. The data in this table shows a wide range of reported values for each of the VOCs due to several reasons. These values represent limits determined by different laboratories using different analytical techniques involving purge-and-trap with packed column GC/MS, packed column GC with Hall or PID detector, or capillary column GC/MS. Also, some laboratories reported minimum detection limits using the EPA's definition (6), while other laboratories reported quantitation limits. Since quantitation limits are usually higher than detection limits, these are conservative numbers.

There are few cases where the reported detection limit was above 0.5 ug/L, the most notable one being a value of 8.5 ug/L for vinyl chloride. This value skewed the average of reported values for this contaminant. More recent data indicate that the original MDL of 8.5 ug/L was not determined properly and that much lower detection limits are achievable using the same analytical method.

## Practical Quantitation Limits

The selection of a concentration that can be achieved reliably with known precision and accuracy is expected to be somewhat higher than the approximate detection limits of 0.2 to 0.5 ug/L. These detection limits are the result of measurement made by experienced laboratories under non-routine conditions and are not expected to be representative of the capabilities of a crosssection of laboratories performing compliance VOC measurements on a routine basis. Further, it has been recommended (6) that if the level of an analyte does not exceed 10 times the MDL, no measured value should be reported. Appendix C explains the rationale used for selection of MCLs for VOCs by defining a term called the practical quantitation limit (PQL) which is somewhat higher than the MDL.

## TABLE 1

## Approximate Method Detection Limits for VOCs

| Compound | Number of Reported Values | Estimated Method Detection Limit (MDL) (ug/L) | Range (ug/L) |
|---|---|---|---|
| Benzene | 8 | 0.2 | 0.03-0.5 |
| Carbon tetrachloride | 9 | 0.2 | 0.08-0.5 |
| p-Dichlorobenzene | 8 | 0.5 | 0.04-2 |
| 1,2-Dichlorobenzene | 9 | 0.3 | 0.02-0.5 |
| 1,1-Dichloroethylene | 8 | 0.2 | 0.05-0.5 |
| Tetrachloroethylene | 9 | 0.3 | 0.05-0.5 |
| 1,1,1-Trichloroethane | 9 | 0.3 | 0.04-1 |
| Trichlorethylene | 9 | 0.2 | 0.02-0.05 |
| Vinyl chloride | 6 | 1.9 | 0.31-8.5* |

*The value of 8.5 ug/L for vinyl chloride was obtained from testing a standard at a concentration of 16 ug/L. This probably led to a deceptively high detection limit.

## Alternative Approaches

Neither EPA method 502.1 nor 503.1 can be used to simultaneously measure all of the VOCs in the MCL proposal. Therefore, these two methods (or method 524.1) will be necessary for compliance monitoring with VOCs regulation unless photoionization and electrolytic conductivity detectors are used in series for the simultaneous determination of volatile halocarbons and aromatics. This approach has been reported previously (7) using a 1% SP-1000 column for the chromatographic separation, and may become more widely used in the future. Also, the use of capillary columns instead of packed columns should improve the resolution between several VOCs and allow the determination of a wider range of purgeables in one chromatographic run. Performance characteristics of new or modified analytical methods will be evaluated as the methods become available.

## Analytical Costs

A survey of analytical costs associated with the analysis of VOCs has been conducted recently (8). This survey included 28 commercial laboratories chosen from those participating in water pollution (WP) and water supply (WS) performance evaluation (PE) studies and which are performing VOC analysis by EPA approved methods.

The average quote for VOC analysis where separate measurements were made for halocarbon and aromatics, using electrolytic conductivity (ElCD) and photoionization detection (PID) was $187/sample and ranged from $75 to $500/sample.

The average cost of VOC analysis using mass spectrometry (MS) was $197/sample, and ranged from $50 to $300.

COST COMPARISON OF VOC ANALYSES

| | GC/MS | GC/ElCD/PID |
|---|---|---|
| Average cost | $197 | $187 |
| Range | $50-$300 | $75-$500 |
| Number of Laboratories | 23 | 13 |

If the lowest and the highest price quotes of each category are excluded, the average cost of a conventional GC analysis becomes $169/sample and the GC/MS analysis $195/sample.

Reducing the number of specific VOCs requiring monitoring did not seriously impact the price of analyses. When asked for a quote to analyze a water for just 10 VOCs as opposed to a complete scan, only 2 of the 13 GC/ElCD/PID laboratories and 3 of the 23 GC/MS laboratories quoted a lower price, an average of $28 less/sample for GC/ElCD/PID and $50 less/sample for GC/MS.

Although not part of the survey, it is possible that some laboratories would simultaneously analyse the VOCs by GC using the PID and the ElCD in series. In that case, laboratory costs may be reduced to about $150/sample. It is expected that the cost per sample will be reduced somewhat once the demand for analysis increases.

Laboratory costs are influenced by the amount of quality assurance. When inquiry about the frequency of laboratories blank analysis was made, the responses of those laboratories surveyed ranged from "every 2 days" to "10% of the samples." Laboratory costs are also influenced by the number of samples the laboratory analyzes on a routine basis. These two factors probably explain the wide range in the laboratory costs.

Overall cost projections of a national monitoring program for VOCs will be made in chapter VII for the proposed compliance monitoring requirements.

## Laboratory Availability

There are approximately 60 laboratories which participate regularly in EPA's Water Pollution performance evaluation studies for VOCs. In addition, there are approximately 200 laboratories which participate regularly in EPA's Water Supply performance evaluation studies for trihalomethanes (THMs). The principles of sample collection and analysis for VOCs are similar to those used for the determination of the four regulated THMs except that the THM MCL (0.10 mg/L) is 1 to 2 orders of magnitude higher than the limits being proposed for seven of the nine VOCs. The selected procedures use equipment and skills available in many drinking water laboratories.

More specifically, Method 502.1 is very similar to the purge-and-trap Method 501.1 for trihalomethanes (9). The recommended primary and secondary analytical columns, the detection system and other chromatographic parameters are the same. Therefore, those laboratories presently using Method 501.1 have the capability to switch to Method 502.1 to measure most of the VOCs of interest. Benzene is the only non-halogenated VOC which has been proposed for regulations and its determination is accomplished by either Method 503.1 or 524.1. Establishment of monitoring requirements for this contaminant may require laboratories to acquire an additional purge-and-trap system with a photoionization detector of a mass spectrometer.

Those laboratories presently using the liquid-liquid extraction (LLE) technique described in Method 501.2 (10) for trihalomethane analyses would probably have to invest in a purge-and-trap system since the LLE technique can only be applied to five of the VOCs. Specifically, Method 501.2 can be extended to include the measurement of trichloroethylene, tetrachloroethylene, carbon tetrachloride and 1,1,1-trichloroethane at concentrations down to 0.5 ug/L, and 1,2-dichloroethane down to 5-10 ug/L (11). At present, there is no detailed write-up on the LLE technique which includes precision and accuracy data for these five compounds.

## ACCEPTANCE LIMITS FOR LABORATORY PERFORMANCE

Each laboratory analyzing samples for compliance purposes must operate a formal quality control program. The minimum requirements of this program for VOCs will be developed by the Drinking Water Laboratory Certification Implementation (DWLCI) Work Group. The available analytical methods for VOCs developed by EMSL-Cincinnati describe procedures which must be followed to establish internal control limits for performance and to monitor continuing laboratory performance. Laboratories must also participate in external performance checks, i.e., WS performance evaluation studies, as required by the laboratory certification program for regulated drinking water contaminants.

These studies are conducted twice per year by the Quality Assurance Branch of EMSL-Cincinnati and participation is required for those EPA and state laboratories wishing to obtain or maintain certification status. Acceptance limits are used to identify those laboratories with poor performance and to help establish the source(s) of deficiencies. Acceptance limits must be developed for VOC analyses in these studies as part of the regulatory process. Only those laboratories able to determine the VOCs within the specified limits will qualify for certification.

Single laboratory, single analyst precision and accuracy data have been obtained and were summarized earlier for each analytical method. A better definition of expected laboratory performance can be obtained from multilaboratory precision and accuracy data. The results from multilaboratory studies account for interlaboratory differences and, therefore, are expected to be more variable than within laboratory results. Multilaboratory data are available from performance evaluation studies for some VOCs.

## Performance Evaluation Studies

Performance evaluation studies are studies which evaluate the ability of laboratories to analyze water samples and to produce data of known quality. The Environmental Monitoring and Support Laboratory in Cincinnati (EMSL-CI) sends participating laboratories a set of sample concentrates with appropriate instructions. Each laboratory produces study samples by diluting a measured quantity of specific concentrates to volume with reagent water, then conducts the analyses, and reports the results to EMSL-CI.

Seven of the nine VOCs in the RMCL proposal have been included in the past in Water Pollution (WP) performance evaluation studies conducted by the Quality Assurance Branch of EMSL-Cincinnati. Participation in WP studies is voluntary, but highly encouraged, since they serve to monitor on a regular basis the ability of a laboratory of produce valid data. The seven VOCs included in WP performance evaluation studies are:

1,2-Dichloroethane
1,1,1-Trichloroethane
Trichloroethylene
Carbon Tetrachloride
Tetrachloroethylene
Benzene
p-Dichlorobenzene

No data from WP studies are available for vinyl chloride and 1,1-dichloroethylene. p-Dichlorobenzene has been included only in recent WP studies and, therefore, data for this compound are somewhat limited.

The analytical methods used to determine these contaminants in WP studies are equivalent to the drinking water methods. Moreover, a recent evaluation of laboratories participating in both WP and Water Supply (WS) studies demonstrated that most of the EPA and state laboratories and many other laboratories analyzing for VOCs in WP studies also analyzed for trihalomethanes in WS studies (12). Therefore, it is reasonable to assume that an evaluation of data from WP studies is a good indication of the performance expected for VOCs if they are added to future WS studies.

The performance data provided by EMSL-CI for WS and WP studies are presented in a format which provides the following types of information:

- Individual analytical results for each participating laboratory. Each laboratory is assigned a code number such that individual results cannot be easily traced back to a particular laboratory.
- Mean and standard deviation for the overall analytical results.
- Number of laboratories using each analytical method.
- Mean and standard deviation by analytical method.

The acceptance limits for laboratory performance in WS studies are presently determined using the following approaches (13). For all regulated contaminants, except trihalomethanes, EPA and state data from past WS studies are used to derive linear relationships relating the reference "true" concentration of the sample to the observed mean recoveries and standard deviations. These linear relationships are used to establish acceptance limits based upon a 95 percent confidence level. (Each study's acceptance limits reflect the most current information on the statistics of the data generated). For trihalomethanes, a criterion of ±20 percent of the reference "true" value is being used to determine acceptance limits.

In WP studies, data falling outside the 95 percent confidence limits are reviewed for problems. However, acceptance limits for laboratory performance are based upon estimates of the 99 percent confidence level using the most recent regression equations.

## An Analysis of Available PE Data from WP Studies

A comparison of acceptance limits for several VOCs in WP study 9 using a 95 percent confidence interval and ±20 percent of the "true" value as acceptance criteria is provided in Table 2. These data indicate that acceptance limits are narrower using ±20 percent of the "true" value than using the 95% confidence interval criterion. Therefore, we would expect that a higher number of laboratories would fail if ±20% of the true value is used for determining acceptability of laboratory performance. This is confirmed in Table 3 which shows the number of laboratories with acceptable data using two different acceptance limits for WP study 9.

## TABLE 2

### Comparison of Acceptance Limits for Several VOCs Study 9 Based upon 95 Percent Confidence Interval and ±20 Percent of True Value

| Contaminant | Sample | True Value (ug/L) | Limits for 95% Confidence Interval | Limits for ±20% of True Value |
|---|---|---|---|---|
| 1,2-Dichloroethane | 1 | 15.9 | 11.3 - 20.9 | 12.7 - 19.1 |
| | 2 | 28.7 | 22.3 - 37.8 | 23.0 - 34.4 |
| Trichloroethylene | 1 | 4.99 | 1.95 - 8.10 | 3.99 - 5.99 |
| | 2 | 21.6 | 16.2 - 27.3 | 17.3 - 25.9 |
| Carbon Tetrachloride | 1 | 6.02 | 2.67 - 8.68 | 4.82 - 7.22 |
| | 2 | 45.2 | 24.4 - 60.5 | 36.2 - 54.2 |
| 1,1,1-Trichloroethane | 1 | 6.42 | 4.02 - 9.06 | 5.14 - 7.70 |
| | 2 | 27.3 | 19.5 - 35.9 | 21.8 - 32.8 |
| Tetrachloroethylene | 1 | 12.2 | 8.27 - 15.4 | 9.76 - 14.6 |
| | 2 | 51.7 | 35.7 - 62.2 | 41.4 - 62.0 |
| Benzene | 1 | 94.1 | 60.0 - 129 | 75.3 - 113 |
| | 2 | 18.8 | 12.0 - 26.0 | 15.0 - 22.6 |

## TABLE 3

### Number of Laboratories with Acceptable Results

| Contaminant | Sample | True Value (ug/L) | Total Number of Participating Laboratories | Percent of labs acceptable at the 95% Confidence Level | Percent of labs acceptable at the 20% of True Value |
|---|---|---|---|---|---|
| 1,2-Dichloroethane | 1 | 15.9 | 57 | 81 | 72 |
|  | 2 | 28.7 | 57 | 82 | 68 |
| Trichloroethylene | 1 | 4.99 | 58 | 90 | 76 |
|  | 2 | 21.6 | 60 | 83 | 78 |
| Carbon Tetrachloride | 1 | 6.02 | 61 | 85 | 59 |
|  | 2 | 45.2 | 62 | 82 | 68 |
| 1,1,1-Trichloroethane | 1 | 6.42 | 61 | 82 | 67 |
|  | 2 | 27.3 | 61 | 75 | 70 |
| Tetrachloroethylene | 1 | 12.2 | 61 | 69 | 61 |
|  | 2 | 51.7 | 60 | 73 | 67 |
| Benzene | 1 | 94.1 | 45 | 76 | 62 |
|  | 2 | 18.8 | 45 | 82 | 67 |

Both approaches have advantages and disadvantages. An argument that could be made in favor of a criterion such as ±20 percent of the true value for VOCs is that it would encourage analytical laboratories to improve their performance since the resulting acceptance limits are stricter. For the trihalomethanes, the limits established in the regulations were based on the performance expected from the "better than average laboratories." Using a percentage of the true value as a criterion results in acceptance limits which are based on the ability of the individual laboratories to perform within the specified limits and not on the overall performance of all the participating laboratories. Since this is a fixed criterion that will be applicable to every study, laboratories will be evaluated always using the same yardstick. However, using this criterion does not take into account the following considerations:

- Recoveries and relative standard deviations may be related to the concentration of the analyte, i.e., the expected performance gets worse as the analyte concentration decreases.
- Since this criterion is based on the "true value," it does not reflect any method bias.
- Since this criterion is fixed, it does not reflect any changes in the state-of-the-art in the analytical methodology.

These three drawbacks are eliminated when a confidence interval approach is used and the statistics from which the limits are calculated are regularly updated to account for changes in quality of data due in part to improvements in analytical methodology. Here the acceptance limits are constructed around the expected mean rather than the "true" value. The resulting limits reflect the performance expected from the "average analyst in the average laboratory". However, the acceptance limits generated using this approach are moving targets which depend on the pool of laboratories participating in each study.

An alternative approach that may be considered for determining acceptability of laboratory performance is using ±20 percent of the true value for higher concentrations and using ±40 percent of the true value at low levels (e.g., ±20% at ≥10 ug/L, ±40% at <10 ug/L). Table 4 summarizes the number of EPA and State laboratories participating in WP studies 8 through 11 outside limits set at ±20% and ±40% of the "true" value of VOC concentrations of 20 ug/L and below. These results are considered to be optimum since they were drawn from experienced laboratories operating under non-routine conditions because they knew they were being tested with standard samples. Actual day to day operations in a wide variety of laboratories using "real" samples would be expected to produce poorer results, i.e., wider performance ranges especially at the lower levels. Data are not available for 1,1-dichloroethylene and vinyl chloride.

## TABLE 4

## Number of Laboratories Outside Acceptance Limits

| | TV | # of labs | # of labs outside $\pm 20\%$ TV | # of labs outside $\pm 40\%$ TV |
|---|---|---|---|---|
| 1,1,1-Trichloroethane | 1.61 | 39 | 16 | 9 |
| | 6.42 | 31 | 6 | 3 |
| | 7.96 | 35 | 8 | 2 |
| | 15.9 | 35 | 6 | 0 |
| Trichloroethylene | 4.99 | 30 | 6 | 3 |
| | 8.32 | 38 | 8 | 2 |
| | 12.0 | 36 | 8 | 2 |
| | 16.8 | 35 | 5 | 2 |
| Tetrachloroethylene | 6.08 | 38 | 11 | 5 |
| | 11.0 | 36 | 4 | 1 |
| | 12.2 | 30 | 6 | 4 |
| Carbon tetrachloride | 6.02 | 31 | 10 | 5 |
| | 10.5 | 35 | 6 | 2 |
| | 12.0 | 40 | 12 | 3 |
| | 16.9 | 37 | 7 | 2 |
| Benzene | 7.10 | 31 | 12 | 6 |
| | 9.4 | 32 | 5 | 2 |
| | 14.1 | 28 | 5 | 1 |
| | 18.8 | 26 | 8 | 4 |
| 1,2-Dichloroethane | 6.43 | 35 | 11 | 3 |
| | 15.9 | 29 | 5 | 3 |
| | 17.1 | 34 | 3 | 0 |
| | 19.1 | 38 | 7 | 3 |
| p-dichlorobenzene | 5.5 | 18 | 5 | 2 |
| | 11.0 | 18 | 5 | 4 |
| | 13.7 | 14 | 8 | 1 |

Notes:
- TV is reference "true" value
- Data taken from WP studies 8 through 11
- Data for EPA and State laboratories only

## Other Available Performance Data

EPA has gathered additional accuracy and precision information from EPA laboratories and contractor laboratories serving EPA (5). Tables 5 and 6 summarize the accuracy and precision information obtained from the analysis of EMSL QC standards at concentration >5-10 ug/L and ≤5 ug/L. These data are limited since EMSL QC standards are not available for vinyl chloride and those laboratories investigated did not report data for p-dichlorobenzene. The information that was obtained for the two concentration ranges had an average accuracy of 84-110% recovery and an average precision of 8-22% relative standard deviation. Average accuracy and precision at these two concentration ranges compare favorably. The information Tables 5 and 6 is very limited since it is based on data from only 2 to 6 laboratories for any given VOC. However, it does indicate that acceptable recoveries and precision are achievable by these laboratories and it indicates that a performance criterion of ±40% of the reference value at concentrations below 10 ug/L is reasonable.

## TABLE 5

### Accuracy Expressed as % Recovery in EMSL QC Samples*

| Compound | Concentration of QC Sample<br>>5 ug/L to 10 ug/L | <br>5 ug/L or less |
|---|---|---|
| Benzene | 92 | 109 |
| Carbon Tetrachloride | 101 | 99 |
| p-Dichlorobenzene | -- | -- |
| 1,2-Dichloroethane | 108 | 84 |
| 1,1-Dichloroethylene | 110 | 106 |
| Tetrachloroethylene | 100 | 100 |
| 1,1,1-Trichloroethane | 96 | 93 |
| Trichloroethylene | 101 | 92 |
| Vinyl Chloride | -- | -- |

*Results summarized in this table are the average of 2 to 6 individual results reported by different laboratories.

## TABLE 6

### Precision Expressed as % Relative Standard Deviation in EMSL QC Samples*

| Compound | Concentration of QC Sample<br>>5 ug/L to 10 ug/L | <br>5 ug/L or less |
|---|---|---|
| Benzene | 8 | 12 |
| Carbon Tetrachloride | 13 | 12 |
| p-Dichlorobenzene | -- | -- |
| 1,2-Dichloroethane | 22 | 14 |
| 1,1-Dichloroethylene | 11 | 13 |
| Tetrachloroethylene | 9 | 12 |
| 1,1,1-Trichloroethane | 10 | 16 |
| Trichloroethylene | 10 | 11 |
| Vinyl Chloride | -- | -- |

*Results summarized in this table are the average of 2 to 6 individual results reported by different laboratories.

## SUMMARY

There are analytical methods available for the determination of VOCs at low ug/L concentrations. These methods involve the use of the purge-and-trap technique and gas chromatography (GC) with a conventional detector or a mass spectrometer (GC-MS). Analytical costs are in the range of $150-$200 per sample. The method detection limits for the nine VOCs are in the range of 0.2 to 0.5 ug/L under optimal laboratory conditions. Both detection limits and quantitation limits are expected to be somewhat higher under routine laboratory operating conditions.

Performance data at low ug/L concentrations indicate good recoveries and good precision. However, data gathered from several sources is generally expected to produce poorer performance at low concentrations. Thus, the selected performance criteria must consider concentration at the analyte. Examples of two approaches for setting acceptance limits that relate performance to concentration are:

1) a statistical approach where regression equations derived from study data are used to establish acceptance limits based upon a percent confidence level; and
2) a percent around the reference "true" value used to establish acceptance limits where the percent around the reference value is related to the concentration of the analyte.

EPA has previously used the following performance criteria with contractor laboratories for the VOCs (based on the second approach described above):

- the reported value must be within ±20% of the reference value for concentrations of 10 ug/L or above, and
- the reported value must be within ±40% of the reference value for concentrations below 10 ug/L.

## V. MONITORING CONSIDERATIONS

The development of compliance monitoring requirements for VOCs must address the selection of samples which are representative of consumer exposure to VOCs in drinking water while still considering the fact that the monitoring requirements must be within the feasible means of water supply systems. The collection of a representative sample involves consideration of where to sample, the number of samples per system and the sampling frequency. The choices depend on the type of source, and the characteristics of the treatment and distribution system used by the CWS. Surface and ground water sources are considered separately because:

1) the sources and mechanisms of contamination for these systems are different,
2) the quality of ground waters tends to change more slowly with time than do surface waters, and
3) ground water contamination is usually a localized problem confined to one or several wells within a system which may be contaminated to different extents.

### Selection of Sample Location

The selection of sample location depends on the type of water being sampled and the reason for sampling (14). The options for selecting sample location are:

1) the water source(s),
2) the water treatment plant or each entry point to the distribution system, and
3) the distribution system.

Monitoring at each of these locations provides useful information. A periodic check of the quality of the water source provides an early indication of contamination incidents and, in some cases, remedial action may be taken before the water is processed (15). Monitoring the quality of the water leaving the treatment plant provides a measure of the effectiveness of process control. Distribution system (DS) monitoring provides a direct measure of the quality of the water reaching the consumer. This latter approach assures that the quality of water at the consumer's tap has not deteriorated in route.

Presumably, VOCs do not form or decompose in the DS. These compounds are not known to be produced as by-products of chlorination in the disinfection process as is the case with chloroform and other related trihalomethanes. Occasionally, however, one or more of these compounds have been detected in treated waters, yet are not present in the source water (16). VOC contamination may be introduced during certain treatment practices. For example, liquid chlorine used in the disinfection process may be contaminated with carbon tetrachloride introduced during the manufacturing process. VOC contamination may also occur in the DS by leaching of materials from pipes and tank coatings. Thus, the potential for VOC contamination exists during treatment and throughout the DS.

It is also possible that VOC concentrations are reduced by treatment practices not originally designed for this purpose. For example, tray aeration was originally designed for $CO_2$ or iron removal, but may in fact remove from 20 to 90% of some

VOCs (17,18). Conventional treatments such as coagulation, settling, softening, and filtration have little to no effect on VOC concentrations.

Ground Water Systems

Sampling the water source may involve monitoring one or more wells within a given system. A large number of ground water systems consist of four or fewer wells. In those systems with more than one well, frequently the water enters the distribution system at two or more different locations. Collection of samples from the water source(s) which are representative of consumer exposure to VOCs is difficult in many ground water systems because:

1) A given well field or aquifer may include one or several wells contaminated by VOCs to different extents, while VOCs may not be present in some adjacent wells,
2) the water volume pumped from each well within a well field is variable,
3) different wells within a system may be used at different times,
4) contamination during treatment or distribution of the finished water is not accounted for, and
5) any treatment process applied by the water supply for the removal of VOCs in the source water is not accounted for.

Sampling at the water treatment plant or at each entry point to the DS would eliminate some of the problems mentioned above. Although this approach would not take into consideration the possibility of contamination during treatment or distribution of the water to consumers, in practice the likelihood of this type of contamination is minimal. Sometimes it might be difficult to identify sampling points for some large systems with multiple entry points to the DS. However, this approach would provide critical information related to which wells within a system may be contaminated.

Sampling one or more locations within the DS provides a more direct measure of consumer exposure to VOCs. This approach is in accordance with the intent of the SDWA which sets drinking water standards for the water which is delivered to the consumer. However, in systems with more than one entry point to the DS, the quality of the water at the tap may vary at different locations within the system. Any monitoring program requiring sampling locations in the DS must take this into account. The sampling points should be distributed accordingly to represent VOC concentrations throughout various portions of the DS.

### Surface Water Systems

The selection of a sample location representative of consumer exposure to VOCs involves similar considerations for surface water systems. Sampling in the DS also provides a more direct measure of consumer exposure to VOCs than sampling the water source or at the treatment plant. As in ground water systems, sampling the water source does not take into account any contamination that can be introduced during treatment or distribution of the water as well as the possible removal of

Ground Water Systems

Determination of the number of sampling points is much more complex for large GWS drawing from multiple wells than for either small GWS or SWS. Obviously, when a single well supplies water to a closed distribution system, the concentration of VOC contaminants should be nearly constant throughout the distribution system. A GWS with multiple wells may need to pump different wells at different rates during peak demand periods of the day. Certain wells in a well field may be on stand-by status, and only run in the event of fire, unexpected demands, or failure of another well. Since water quality might not be the same in all wells in a particular well field, the number of wells pumping and the relative pumping rates can affect the concentration of VOCs in the blend of DW reaching the consumer. Certain treatments applied to the water (especially GAC and aeration) can reduce the concentration of VOCs reaching the consumer (20).

Mixing of waters containing different concentrations of VOCs occurs when well water is pumped to a common storage tank or a treatment plant. Treatment plants using chemical addition processes such as coagulation or softening should be designed for complete mixing of the incoming water as will some plants using aeration. Water from various wells entering a common storage tank may be either partially or completely mixed. Complete mixing might occur if the conveyance pipes meet at some juncture other than the tank. Little mixing will occur if the various well waters enter the storage tank at different points. Also, some designs allow individual services to homes to draw off the water main between the well and the tank, others do not. Even with mixing there may be periods of different exposures caused by alternate pumping from contaminated and uncontaminated wells. Exposure from a highly contaminated well may sometimes go undetected due to large dilution effects from less contaminated wells.

### Surface Water Systems

The number of sampling points for SWS is determined by the number of sources and the number of treatment plants within the system. The number should be such as to be qualitatively and quantitatively representative of each water source. In situations where a system has two treatment plants drawing water from the same source, via the same intake, the plants may be treated as one for the purpose of determining the number of sampling points if the two plants have similar treatment processes.

## Sampling Frequency

The selection of sample collection frequency and sampling points are both connected to the potential variability of the water delivered to the consumer. Collection frequency concerns mostly time-related changes in water quality while collection points relate more to variability caused by changes in mixing or distribution of different sources within the system. In general, for SWS the variability in water quality with time is more important that variability within the system. Factors such as run-off rates, seasonal variations, weather, and watershed area and use are important considerations for SWS. The collection of several samples throughout the monitoring period would provide a better indication of long term exposure than one sample would. For ground water systems, contamination problems are usually more localized in nature and may be limited to one or several wells. Thus, the number and location of collection points within the system are important factors in obtaining representative samples in ground water systems particularly for those systems using multiple wells. The collection of samples at different locations throughout the system would provide an indication of where contamination may occur.

## Vulnerability of CWS

VOC contamination has been measured in many ground and surface water sources. While no one factor adequately predicts VOC occurrence in a sample, proximity to VOC use increases its probability. This predictability can be improved by considering the extent of protection afforded the drinking water source by land-use programs or natural factors.

This discussion suggests VOC vulnerability criteria that can be used to designate an order in which to phase CWS into a compliance monitoring program. A detailed analysis of occurrence information used to develop VOC vulnerability criteria is provided in Appendix A. Although technical information alone is insufficient to determine which CWS to include in such a program, it does show that it is very difficult to prove that a system is not vulnerable to VOC contamination. For example, nonoccurrence of VOCs in a sample is not adequate proof of nonvulnerability (21); whereas occurrences may indicate a current or future drinking water quality threat. This is because it is difficult to select a small number of samples that provide a representative time-average of consumer exposure to VOCs.

To occur in consumer tap water samples, VOCs must:

1) be present in the environment as determined by monitoring data or predicted by a vulnerability assessment,
2) infiltrate water sources by seepage into a ground water, or by runoff or discharge into a surface water, and
3) move through the source into finished drinking water as evidenced by knowledge of drinking water movement, environmental persistence of VOCs, and water treatment practices.

These three factors, combined with an analysis of VOC occurrence trends, lead to proposing the following criteria that may be used singly, or in combination to rate VOC vulnerability of water sources. These criteria are:

1) size of the population served by the utility,
2) nearby use of VOCs, and
3) protection of the DW source.

The last two criteria apply to each aquifer or surface water used by the CWS. The population criterion is independent of the number, type or quality of waters used. In some ways, it is also the most interesting and useful. For example, including all large, pop. >3300, CWS in a compliance monitoring requirement would cover 78% of the U.S. population. Discussion of these vulnerability criteria follows.

### Criterion 1: Population

Nearby use of VOCs, which correlates positively with population served by the CWS, has been linked to occurrences in drinking water sources. If all CWS serving populations larger than 3300 were considered vulnerable, approximately 3400 surface and 3500 ground water systems would be judged vulnerable. To rank the remaining CWS (populations served, ≤3300), the following can be considered:

1) previous measurements of VOCs in tap, well or nonpotable water samples. These occurrences indicate a presence of VOCs in the source that may later contaminate potable water supplies.
    a) For surface waters, the presence may be the result of sporadic discharges that need to be characterized with respect to frequency, duration and extent.
    b) Contamination of ground water samples may indicate a highly contaminated well in the wellfield, low concentration contamination of all the drinking water wells, or just sporadic effects from an occasionally polluted recharge zone.
2) Proximity of a smaller system to a larger community may increase the vulnerability of the smaller system because nearby dumping into surface waters, or into ground water recharge areas, can contaminate local drinking water supplies.

  - a) Proximity of a surface water system to a larger community can be defined in terms of the flow rates between the monitoring points.
  - b) Proximity is harder to define for ground water systems; possibilities include:
    - i) determining hydraulic gradients and travel times between the smaller CWS well(s) and the contamination source. Ground water modeling can be useful, especially when the geology or the well field pumping patterns are complex or uncertain (22).
    - ii) defining "nearby" statistically, by means of Standard Metropolitan Statistical Areas.

3) Other factors that define vulnerability of a CWS to VOC contamination could be included at the discretion of the States.

Criterion 2: Nearby Use of VOCs

A hierarchy of use can be established for a state or regional watershed area or groundwater basin.

High volume use: metal fabricators, solvent producers, electroplating plants, airfields, military bases, Superfund sites, closed wells, and a history of large spills are all indicators of the potential for significant presence of VOCs in or near drinking water sources.

Light volume use: electronic component, dry cleaner and small commercial users, protected surface impoundments are examples. Agricultural areas need to be identified primarily for pesticide and herbicide monitoring, but the VOC, 1,1,1-trichloroethane, is a solvent for some agricultural chemicals.

It is likely that more than one of these use categories will apply to the area served by a single CWS. The effect of each on the nearby drinking water sources (surface or ground) will have to be evaluated. As with occurrence data, evidence of use is more informative than absence. The latter can be difficult to determine, and the former indicates a potential problem.

## Criterion 3: Protection of the Water Source

The source may be protected by natural factors or discharge controls.

### Surface Water Sources

A sanitary survey and an examination of registered pollutant dischargers can indicate the nature and extent of pollution activities that affect the vulnerability of a surface water system. Some watersheds are protected by strict access and land use laws, which are easier to police than corresponding (e.g. UIC) ground water protection programs.

Surface water systems could be ranked according to the extent of watershed protection afforded by either these land-use restrictions or the remoteness of the source from VOC-based activities. This could be especially effective in rating the vulnerability of the 7700 small, pop. $\leq$3300, surface water systems.

## Ground Water Sources

Ground water sources can be protected naturally by geological formations above the aquifer that are impermeable to VOCs used or stored near the surface, or by strict aquifer management practices. Two problems exist: first, even geologically invulnerable formations can be polluted by improper well construction or dumping into existing wells. Second, because of the complex nature of ground water hydrogeology it is difficult to regulate and monitor land-use as effectively as for surface water sources.

Rating the vulnerability of ground water systems will often require simultaneously considering aquifer protection and nearby use of VOCs. It is important to characterize the recharge areas by:

- locating industrial, commercial or municipal facilities that handle wastes or use solvents,
- identifying geological materials that are porous, fractured or have solution openings near VOC sources that overlap the cones of influence of DW wells, and
- locating abandoned wells, which can be a sign of faulty well construction, an opportunity for improper dumping, or the existence of a contaminated well.

## Summary

Characteristics of ground and surface water sources and systems have been examined for probable mechanisms of VOC contamination of drinking water. Surface waters are generally more variable in quality, and less protected from contamination than ground water sources. Contamination causes are easier to identify, follow and control in surface waters than in ground waters. Ground water quality tends to vary slowly, but once contaminated the source can pose a long-term threat to drinking water supplies. Finished drinking water can be contaminated by impurities in water treatment chemicals, or by VOCs introduced directly or indirectly within the distribution system.

Occurrence data collected in several surveys over the past decade has been examined for trends that indicate a predictable pattern of VOC occurrences. (See Appendix A.) Because the site selection criteria, analytical methodology and other key factors differed greatly between these surveys, no reliable trends were established.

However, from these trends and our knowledge of possible VOC contamination mechanisms, three broad criteria that help predict the relative vulnerability of CWS to VOC contamination have been suggested. These criteria provide part of the basis for the phasing-in schedule proposed in the compliance monitoring requirements. These criteria can be applied separately to ground and surface water sources, and include determining:

1) the size of the populations served by contiguous CWS,
2) the nature and extent of VOC use in the area, and
3) the extent of protection of the drinking water source by natural or regulatory causes.

## VI. MONITORING FOR UNREGULATED VOCs

EPA is considering the development of monitoring regulations that will require public water systems to monitor for unregulated contaminants in drinking water. This action will be taken under the authority of section 1445(a) of the SDWA which states that, "Every person who is a supplier of water, . . . shall establish and maintain such records, make such reports, conduct such monitoring, and provide such information as the Administrator may reasonably require by regulation to assist him in establishing regulations, . . . in evaluating the health risks of unregulated contaminants, or in advising the public of such risks." The main objectives of this regulation will be consistent with the goals of section 1445(a), as follows:

- To assess the extent of contamination and human exposure to other contaminants not currently under consideration for inclusion in the Revised Regulations (i.e., unregulated contaminants).
- To accelerate compliance monitoring for the contaminants to be included in the Revised Primary Drinking Water Regulations.

To date, only a small percentage of water supplies have actually sampled their water to assess the extent of contamination by VOCs and other organic contaminants. Monitoring is currently not being conducted in a comprehensive manner by public water systems which would serve to alert the public to potential health risks in their drinking water and the need for remedial action. Drinking water standards and compliance monitoring would provide some measure of protection but implementation of standards are several years away and will not cover all possible contaminants in drinking water.

## Background

The assessment of the quality of drinking water in the U.S. has been accomplished through various monitoring activities including: (1) compliance monitoring for the drinking water standards, (2) EPA-conducted national statistically designed surveys of selected drinking water supplies, (3) State surveys, (4) responses to incidences of contamination, and (5) research studies. As a result of these monitoring activities, numerous organic chemical contaminants have been found over the last few years including VOCs, pesticides, disinfection by-products, and other synthetic organic chemicals. Widespread contamination potential of public water supplies has been determined to exist through these monitoring efforts. For example:

- About 20 percent of public water systems detected at least a trace of volatile organic chemicals (VOCs) in the 1,000-city ground water survey.
- Sampling of ground waters around hazardous waste sites has identified many synthetic organic chemicals (SOCs) that threaten public water supplies.
- Pesticides in ground and surface waters are the most recent concern as various pesticides have been detected in water supplies across the country; e.g., aldicarb, DBCP, EDB, and alachlor.

However, the extent of contamination of ground and surface waters is unknown for many CWS. A systematic and comprehensive monitoring program would make these systems aware of possible contamination and would determine the quality of drinking water in CWS across the country.

Major interest in a monitoring program was shown by Congress last year when legislation was nearly enacted to require monitoring for unregulated organic chemicals. During 1984, congressional debate focused on the need for more occurrence data for standard setting and for widespread monitoring of unregulated contaminants. The intent of the monitoring requirements discussed by the Congress was: (1) elevate public awareness regarding the quality of their drinking water and (2) identify problems of gross contamination for immediate remedial action by State and local authorities. In Congress' view, requiring monitoring would stimulate interim measures for public health protection until drinking water regulations could be promulgated.

EPA sponsored a workshop in November 1984 to discuss the need for and specific aspects of possible monitoring regulations for unregulated contaminants in drinking water. Representatives of States, utilities, public interest groups, analytical laboratories, and consultants attended the workshop. The work group which discussed monitoring regulations for VOCs concluded that EPA should proceed with development of monitoring regulations for 40 to 50 VOCs at all public water systems.

The National Drinking Water Advisory Council (NDWAC) considered this issue in its December 1984 meeting and recommended that a systematic national monitoring program for unregulated VOCs and pesticides/SOCs be implemented. The NDWAC emphasized the need for VOC monitoring and monitoring for a limited number of pesticides for which sufficient analytical capabilities existed. Monitoring regulations for other pesticides/SOCs would follow as methods/data become available.

Which VOCs?

Two approaches could be taken in the selection of specified VOCs to be included in a monitoring regulation. The first and most comprehensive approach is to include approximately 60 VOCs that are detected using the purge and trap gas chromatography techniques described in Chapter IV. Table 7 provides a list of the VOCs that can potentially be included in a monitoring regulation. The second approach is to include only those VOCs which may be of concern because of their possible occurrence in drinking water supplies and potential adverse health effects of human exposure. The monitoring efforts in any regulatory activity should be limited to those chemicals that have been detected or are likely to occur in drinking water and that may pose an adverse health risk. This approach was recommended by the members of the VOCs work group during the November 1984 workshop on monitoring regulations. However, unidentified peaks should not be ignored and efforts should be made for identification, whenever possible, of any additional peaks which show up in a chromatogram. Table 8 provides

provides a list of VOCs which may be considered for a monitoring regulation using the second approach. The compounds have been selected based on present regulatory interest and available occurrence information. The compounds included are:

- four trihalomethanes in the November 29, 1979 Federal Register;
- additional VOCs being considered for later phases of the Revised Regulations;
- VOCs not included above but detected in the Ground Water Supply Survey and various Federal and State surveys; and
- VOCs that have potential for occurrence in drinking water; VOCs detected in waste waters, surface or ground waters or have widespread dispersive use patterns and high production.

## Analytical Considerations

The VOCs can be measured in a single analysis by GC/MS or by up to three separate analyses using GC. Estimated costs are $150 to $200 for the GC/MS and about $100 per GC analysis. The three analyses include:

A Purgeable halogenated hydrocarbons
B Purgeable aromatics
C Requires low limits of detection (sub-ppb levels)

Analysis of certain highly volatile substances (e.g., fluorotrichloromethane) can be incorporated into the procedures for other purgeable halogenated hydrocarbons through minor adaptations (e.g., change in the trapping device). Otherwise,

# TABLE 7

## VOCs that Can Be Analyzed by Purge and Trap GC

*Chloromethane
*Bromomethane
*Vinyl chloride
Fluorotrichloromethane
Bromochloromethane
trans-1,2-Dichloroethylene
Chloroform
*Dibromomethane
Carbon tetrachloride
Bromodichloromethane
1,1-Dichloropropane
*1,2-Dibromoethane
2-Chloroethylvinyl ether
1,2,3-Trichloropropane
1,1,2,2-Tetrachloroethylene
Chlorobenzene
*1,2-Dibromo-3-chloropropane
o-Chlorotoluene
m-Dichlorobenzene
p-Dichlorobenzene
Toluene
p-Xylene
o-Xylene
n-Propylbenzene
p-Chlorotoluene
1,3,5-Trimethylbenzene
p-Cymene
*Cyclopropylbenzene
*1,2,3-Trichlorobenzene
1,1,1,2-Tetrachloroethane
Dichloroethane
Trichloroethylene
Dichlorodifluoromethane
Chloroethane
1,1-Dichloroethylene
1,1-Dichloroethane
cis-1,2-Dichloroethylene
1,2-Dichloroethane
1,1,1-Trichloroethane
1,2-Dichloropropane
1,1,2-Trichloroethane
2-Chloroethylethyl ether
Bromoform
1,1,2,2-Tetrachloroethane
*Pentachloroethane
1-Chlorohexane
Bromobenzene
bis-2-Chloroisopropyl ether
o-Dichlorobenzene
Chlorodibromomethane
Benzene
Ethylbenzene
m-Xylene
iso-Propylbenzene
tert-Butylbenzene
sec-Dichloropropane
1,3-Dichloropropane
1,2,4-Trimethylbenzene
n-Butylbenzene
*Napthalene
*1,2,4-Trichlorobenzene
*Styrene

*Potential problems in analysis.

## TABLE 8

## VOCs UNDER CONSIDERATION FOR MONITORING REGULATIONS

| | |
|---|---|
| A | Chloroform |
| A | Bromodichloromethane |
| A | Chlorodibromomethane |
| A | Bromoform |
| A | trans-1,2-Dichloroethylene |
| A | Chlorobenzene |
| A | m-Dichlorobenzene |
| A | Dichloromethane |
| A | cis-1,2-Dichloroethylene |
| A | o-Dichlorobenzene |
| A | 1,2,4-Trichlorobenzene |
| A | Fluorotricloromethane |
| A | Dichlorodifluoromethane |
| A | Dibromomethane |
| C | 1,2-Dibromoethane (EDB) |
| C | 1,2-Dibromo-3-chloropropane (DBCP) |
| B | Toluene |
| B | p-Xylene |
| B | o-Xylene |
| B | m-Xylene |
| A | 1,1-Dichloroethane |
| A | 1,2-Dichloropropane |
| A | 1,1,2,2-Tetrachloroethane |
| B | Ethylbenzene |
| A | 1,3-Dichloropropane |
| B | Styrene |
| A | Bromobenzene |
| B | Benzene |
| A | p-Dichlorobenzene |
| A | 1,1-Dichloroethylene |
| A | Chloromethane |
| A | Bromomethane |
| A | Bromochloromethane |
| A | 1,2,3-Trichloropropane |
| B | 1,2,3-Trichlorobenzene |
| B | n-Propylbenzene |
| A | 1,1,1,2-Tetrachloroethane |
| A | Chloroethane |
| A | 1,1,2-Trichloroethane |
| A | Pentachloroethane |
| A | bis-2-Chloroisopropyl ether |
| A | sec-Dichloropropane |
| B | 1,2,4-Trimethylbenzene |
| B | n-Butylbenzene |
| B | Napthalene |
| B | Hexachlorobutadiene |
| B | o-Chlorotoluene |
| B | p-Chlorotoluene |
| B | 1,3,5-Trimethylbenzene |
| B | p-Cymene |
| A | 1,1-Dichloropropane |
| B | iso-Propylbenzene |
| B | tert-Butylbenzene |
| B | sec-Butylbenzene |
| A | Trichloroethylene |
| A | Tetrachloroethylene |
| A | Carbon tetrachloride |
| A | 1,1,1-Trichloroethane |
| A | 1,2-Dichloroethane |
| A | Vinyl chloride |

NOTE:

A -- Can be analyzed using the Purgeable Halogenated Hydrocarbon Method
B -- Can be analyzed using the Purgeable Aromatic Hydrocarbon Method
C -- Of concern at very low levels (requires low limit of detection)

four separate analyses would be required. Monitoring for EDB and DBCP (category C) requires special analysis estimated to cost an additional $50.00 per sample. Analysis of category C compounds is more difficult than for other VOCs. Only those laboratories experienced in these analyses should be considered to perform analyses for monitoring regulations. One option to consider is that such analyses be required only for systems considered vulnerable to contamination by these chemicals. This approach would limit the number of samples so that only highly qualified laboratories would be involved in these analyses.

Monitoring for unregulated VOCs should be performed by experienced laboratories to produce data of known and high quality which may be later used to support regulatory decisions. Preferably, the analyses should be performed by the existing network of laboratories which are certified for trihalomethane analyses. The laboratories should document the quality of VOC data by following an internal quality control plan which includes as a minimum the quality control measures specified in the analytical methods (e.g., calibration standards, quality control samples) and by obtaining acceptable performance in performance evaluation studies. These minimum requirements are recommended for "interim" certification of the laboratories until such time when a full certification program becomes effective if such analyses are to be used for compliance with MCLs for regulated VOCs.

The recommended procedures for sample preservation and storage for VOCs depend on whether one or more samples are collected for analysis at each sampling site and the specific VOCs of interest. Volatile aromatic compounds are sensitive to biological activity and must be acidified or refrigerated during shipment and must be kept refrigerated until analysis. Volatile halogenated halocarbons can be preserved with sodium thiosulfate and shipped at ambient temperatures. Also, these compounds can be preserved with acid or refrigeration as described for the volatile aromatic compounds. Those systems that chlorinate may need a minimum of two samples if the trihalomethanes and styrene (which reacts with chlorine) are to be measured. One sample would be preserved with sodium thiosulfate (or sodium sulfite) to quench the chlorine residual while the second sample would be preserved by acidification and refrigeration. The recommended maximum holding time for preserved samples is 14 days from the time of collection. However, additional research is needed in the areas of sample preservation and storage to minimize losses prior to analysis. Also, the feasibility of adding both a reducing agent and acid simultaneously to one sample to decrease the number of samples required needs further investigation.

## Proposed Monitoring Requirements

Because similar analytical procedures for the nine VOCs can also measure numerous other VOCs at relative small additional costs, monitoring regulations are being developed simultaneously for other VOCs. Three different monitoring options have been considered for the unregulated VOCs. The options ranged from an extensive federally mandated specific monitoring program to a monitoring program whose specifics (e.g., repeat monitoring) would be largely determined by the States. The proposed monitoring requirements for the second option are similar to those proposed for compliance monitoring in Chapter II so that systems will be allowed to use the same samples for analysis of both the other VOCs in Table 8 and the nine VOCs for which MCLs are being proposed. This monitoring program provides reasonable minimum federal requirements with provisions for State discretion in their application. Thus, Option 2 is recommended for maximum use of available resources (e.g., laboratory capabilities, cost effectiveness). In addition, provisions should be made for "grandfathering" previous data of acceptable quality to maximize cost effectiveness. The three options for minimum federally mandated monitoring requirements outlined below generally correspond to the three options described earlier for compliance monitoring for the nine VOCs.

Option 1. This option proposes relatively stringent monitoring require ments and includes minimum repeat monitoring for all systems. The monitoring program will be phased in over a four year period based on the size of the population served by the CWS in a similar manner as described under Option 1 of the proposed compliance monitoring requirements. Ground water systems would be required to sample quarterly for one year in the distribution system at points representative of each source. All systems would be required to resample positive samples. All systems would be required to repeat monitoring every 10 years.

## TABLE 9

## PROPOSED MONITORING REQUIREMENTS FOR UNREGULATED VOCs

### Initial Monitoring

- All systems monitor once over four years
- Requirements are by system size:

| Size of System | Complete by End of |
|---|---|
| >10,000 | 1 year |
| 3,300-10,000 | 2 years |
| <3,300 | 4 years |

- Ground Water Systems: One sample per well at each entry point to the distribution system
- Surface Water Systems: Quarterly samples per each source for one year at points in distribution system representative of each source

### Repeat Monitoring

- State discretion for repeat sampling; dependent upon vulnerability and results of first round of monitoring.

Option 2. This option is the same as Option 1 above except that it provides for State discretion on resampling positive results and on repeat monitoring requirements. Table 3 presents presents the proposed requirements.

Option 3. Under this option all systems would monitor once over a five year period. Monitoring would be phased-in by the size of population served by the CWS as described under Option 3 of the compliance monitoring requirements. Ground water systems would be required to sample only 25 percent of their wells and the sampling would be done at the well head. The State would have discretion on whether to require confirmation samples. Also, States would have discretion on whether to require surface water systems to monitor based upon a vulnerability assessment. There is no repeat monitoring requirement under this option. Estimated additional monitoring costs for the three options are summarized in Table 10. These monitoring costs assume that monitoring for VOCs will be conducted simultaneously. Thus, only additional costs incurred by monitoring for unregulated VOCs are shown here. Detailed calculations are presented in the next chapter.

TABLE 10

ADDITIONAL COSTS FOR MONITORING OF UNREGULATED VOCs

| | Option 1 | Option 2* | Option 3** |
|---|---|---|---|
| Initial Round | $2.7 million | $2.3 million | $0.6 million |
| Repeat Monitoring | $2.7 million | $0 million | $0 million |

*Over 4 years

*Over 5 years

## Summary

The lead option for monitoring of unregulated VOCs has provisions for the use of such data for compliance purposes with the MCLs for the nine VOCs. This approach would minimize the monitoring costs of the regulation. Minimum requirements to assure that the data are of known and high quality have been recommended. There are no minimum federal requirements for repeat monitoring of unregulated VOCs under the lead option. States are expected to play a major role in repeat monitoring and other follow-up activities after the first round of sampling.

# VII. MONITORING COSTS

Calculation of the national monitoring costs associated with the proposed regulations for VOCs in drinking water requires the consideration of many factors. The monitoring cost estimates summarized in this chapter for the three monitoring options described in chapters II and VI have been based on a number of assumptions. The accuracy of these cost estimates is directly related to the accuracy of the assumptions made during the calculations. There is a degree of uncertainty inherent in any assessment of costs. The likely magnitude of the errors in the national estimates of overall compliance costs (including costs of contamination removal) are discussed elsewhere (23). A fundamental source of uncertainty in the monitoring cost estimates arises from the fact that only a small number of observations are available to determine the frequency and degree of contamination from any given VOC. The result is that extrapolation is made from limited occurrence information to specify the likely number of systems affected by this regulation.

Additional assumptions contributing to the overall uncertainty of the monitoring cost estimates include the following:

- The source used to estimate the number of ground and surface water systems in the United States is the Federal Reporting Data System (FRDS). The error of these figures is unknown.
- It was assumed that surface water systems have one source on the average.

- It was assumed that for ground water systems the average number of wells varied with the size of the population served by the system in the following manner:
  - >10,000 people, 10 wells/system
  - 10,000 - 3,300 people, 8 wells/system
  - <3,300 - 500 people, 4 wells/system
  - <500 people, 2 wells/system
- The analytical costs per sample were estimated at $150 for compliance monitoring and $200 for unregulated VOCs.
- It was assumed that systems will analyze simultaneously for compliance and for unregulated VOCs. Therefore, the monitoring costs for the unregulated VOCs only show the additional cost of the monitoring regulation. The additional cost was estimated at $50 per sample ($200 versus $150 for unregulated and compliance monitoring, respectively).
- Additionally, it was estimated that about 20% of the systems would be required to analyze for ethylene dibromide (EDB) and dibromochloropropane (DBCP) at an increased analytical cost of $50 per sample.
- Ground water systems will sample at each entry point to the distribution system. It was assumed that ground water systems serving a population above 3,300 have one entry point per every 2 wells while those serving a population of 3,300 or less have one entry point per well. The minimum number of samples is one per each entry point.
- To estimate the costs for repeat monitoring the following assumptions were made:

  - 30% systems >3,300, VOCs are detected
  - 15% systems <3,300, VOCs are detected
  - 60% systems >3,300, are vulnerable
  - 20% systems <3,300, are vulnerable
- When confirmation of positives is required, it was estimated that about 20% of the systems will have positives. This percent is in agreement with results from the GWS.

The monitoring cost estimates for each option described in chapters II and VI are summarized in Table 11. These cost estimates do not include any additional cost impact due to more stringent monitoring requirements imposed by individual States. Therefore, for purposes of these calculations, when there is State discretion in the specific monitoring requirements, the estimated cost was zero.

Detailed calculations for the summary provided in Table 11 are given elsewhere (24).

TABLE 11

Costs for Monitoring for Compliance and for Unregulated VOCs*

| Initial Round | Option 1 | Option 2 | Option 3 |
|---|---|---|---|
| Compliance | $25 million/yr | $9.3 million/yr | $3.8 million/yr |
| Unregulated | $2.7 million/yr | $2.3 million/yr | $0.5 million/yr |
| **Repeat Monitoring** | | | |
| Compliance | $63.7 million/yr | $17.4 million/yr | $2.9 million/yr |
| Unregulated | $2.7 million/yr | $0 | $0 |

*This table shows only the additional costs incurred if unregulated VOCs are determined with compliance samples.

# REFERENCES

1. Horwitz, W.J. Assoc. Off. Anal. Chem., Vol. 65, No. 3, pp. 525-530 (1982).

2. EPA, Method 502.1, "Volatile Halogenated Organic Chemicals in Water by Purge and Trap Gas Chromatography," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (1985).

3. EPA, Method 503.1, "Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (1985).

4. EPA, Method 524.1, "Volatile Organic Compounds in Water by Purge and Trap Gas Chromatography/Mass Spectrometry," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (1985).

5. EPA, May 8, 1985 memorandum from R. Kent Sorrell to Maria Gomez-Taylor.

6. Glaser, J.A., et al., Env. Sci. and Tech., Vol. 15, No. 12, pp. 1426-1435.

7. Kingsley, B.A. et al, "Gas Chromatographic Analysis of Purgeable Halocarbon and Aromatic Compounds in Drinking Water Using Two Detectors in Series," Chapter 41 in Water Chlorination.

8. EPA, November 21, 1984 memorandum from R. Kent Sorrell to Maria Gomez-Taylor.

9. EPA, Method 501.1, "The Analysis of Trihalomethanes in Drinking Water by the Purge and Trap Method," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (1979).

10. EPA, Method 501.2, "The Analysis of Trihalomethanes in Finished Water by the Liquid/Liquid Extraction Method," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (1979).

11. Glaze, W.C. and Lin C. -C., Optimization of Liquid-Liquid Extraction Methods for Analyses of Organics in Water, EPA-600/54-83-052, January 1984.

12. EPA, June 1, 1983 memorandum from Paul W. Britton to Maria Gomez-Taylor.

13. EPA, November 16, 1984 memorandum from Paul W. Britton to EPA's Quality Assurance Officers.

14. AWWA, Principles and Practices of Water Supply Operations, Volume 4: Introduction to Water Quality Analyses, pp. 23-42 (1982).

15. EPA, Committee on the Challenges of Modern Society (NATO/CCMS), Drinking Water Pilot Study Summary, EPA 570/9-82-007 (1983).

16. Love, Jr., O.T., and Eilers, R.G. JAWWA *74*, 8: 413-425 (1982).

17. Love, O.T., and Miltner, R.J. 1982. Removal of Volatile Organic Contaminants from Ground Water by Adsorption. Proceedings, First Atlantic Workshop on Organic Contamination of Ground Water Supply Association. Nashville, Tennessee. December 1982.

18. Hess, A.F., Dyksen, J.E., and Cline, G.C. Case Studies Involving Removal of Organic Chemical Compounds from Ground Water. Paper Presented at the Pre-conference Seminar Concerning Organic Chemical Contaminants in Ground Water at the 1981 Annual Conference of the American Water Works Association, St. Louis, Missouri, June 7-18, 1981.

19. EPA, Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA-600/4-82-029, September 1982

20. Dyksen, J.E., and Hess, A.F., JAWWA *74*, 8: 394-403 (1982).

21. Scalf, M.R. *et al*., *Manual of Ground Water Quality Sampling Procedures*, NTIS # PB 82-103045.

22. Keith, S.R., *et al*. Ground Water Monitoring Review *3*, 21-30 (1983).

23. EPA, Regulatory Impact Analysis for VOCs, Office of Drinking Water, May 1985 (EPA 570/9-85-004).

24. EPA, May 10, 1985 memorandum from Joseph A. Cotruvo to Arnold M. Kuzmack.

# APPENDIX A

## Relative Vulnerability of CWS

The rationale for monitoring all CWS at least once, and for phasing this monitoring in over a period of time were suggested in Chapter V. The purpose of this appendix is to suggest criteria for rating the relative vulnerability of CWS to VOC contamination. This ranking system provides a basis for the phasing-in schedule that is outlined in the CMR in Chapter V. Water sources, not water utilities, are emphasized since this permits consideration of ground and surface water characteristics separately, and avoids the difficulty of dealing with CWS that use both types of sources.

This appendix first considers:

1) characteristics of SW and GW sources that could lead to contamination or protection of a drinking water source, and
2) trends, in available occurrence data, that indicate a connection between VOC occurrences and factors such as population, nearby presence of industrial/commercial users, or the degree of watershed and recharge zone protection afforded the DW source by natural or regulatory causes.

Next, three criteria for ranking the relative vulnerability of a group of CWS within a region or state, are suggested:

1) natural or regulatory protection of the DW source,
2) nearby use of VOCs, and
3) the size of the population served by the CWS.

## Surface Water Characteristics

Lakes, reservoirs, streams, rivers or other surface water sources are used by approximately 20% of the nations' CWS to provide drinking water to about 65% of the population. Surface waters are often classified as protected or unprotected sources. Sources in remote regions that are fed from rainfall, snow melt and other pristine sources are protected; some mountain reservoirs are examples of these. Rivers and lakes in populated or industrialized regions that are subject to agricultural or municipal runoff, or industrial discharges are unprotected sources. The Ohio and Mississippi Rivers and industrialized regions of the Great Lakes are examples of unprotected surface water sources.

The most likely causes of VOC contamination of surface waters are industrial discharges or spills. The latter are difficult to predict, but the former can be located by physical inspection. Also, the NPDES program provides a record of quantities and types of chemicals directly discharged into surface waters. Some of the industries that use VOCs in the production, fabrication or manufacture of: electronic or metal components, cosmetics, textiles, food, pesticides, adhesives, lubricants, PVC, drain cleaners or fluorocarbons are listed in Table 1.

Table 1

Industries That Use VOCs

| Industry/Subcategory |
|---|
| Aluminum Forming Industry |
| Battery Manufacturing Industry |
| Coal Mining Industry |
| Coil Coating Industry |
| Copper Forming Industry |
| Electronic Components Industry |
| Foundries Industry |
| Inorganic Chemicals Industry |
| Iron and Steel Industry |
| Leather Tanning and Finishing Industry |
| Metal Finishing & Electroplating |
| Nonferrous Metals Industry |
| Ore Mining and Dressing Industry |
| Organic Chemicals & Plastics Industry |
| Pesticides Industry |
| Petroleum Refining Industry |
| Pharmaceuticals Manufacturing Industry |
| Porcelain Enameling Industry |
| Pulp and Paper Industry |
| Textile Industry |

Agricultural and municipal surface runoffs are nonpoint discharges that can be sources of pesticides and polynuclear aromatic compounds, respectively; but they are unlikely to contain large amounts of the nine VOC contaminants. Rainfall and water from groundwater recharge or surface water confluences may have dilution effects.

Surface waters are subject to the beneficial effects of air, sunlight and aerobic organisms that can remove or decompose organic contaminants. The removal effect, especially in rapidly flowing sources, can be significant for volatile, relatively water-insoluble VOCs like carbon tetrachloride and tetrachloroethylene (1). Biodegradation of benzene, and perhaps other VOCs, is also possible (2-4). These self-cleaning mechanisms will vary seasonally, and from source to source. For example, an ice covering can significantly decrease the rate of VOC volatilization (5).

The VOC concentrations in fast-flowing surface waters may change greatly with time, and spills can be tracked. These types of surface waters are less likely to have persistent gross contamination at a given withdrawal point; however, sporadic spills can and have caused consumer exposure to high concentrations of VOCs in drinking water for short durations (6).

The Huntington Water Company monitoring of their raw (Ohio River) water source shows (Table 2) that contamination levels can remain static for weeks, and then increase quickly by an order of magnitude (7). The chloroform contamination is in the raw water as a result of upstream discharges or spills, not as a result of any synthesis from chlorination practices.

## Table 2

### Variability at a Fixed Withdrawal Point at Huntington, WV Water Corporation: Analysis* of Raw (Ohio River) Water Samples

| JAN - JUL 1978 Sampling Date | Chloroform | Benzene | Dichlorobenzene isomers | Carbon Tetrachloride |
|---|---|---|---|---|
| 1/17 | 4.3 | ND | 0.4 | 0.8 |
| 1/31 | NA | ND | ND | NA |
| 2/9 | 2.3 | ND | ND | 0.8 |
| 2/16 | 0.6 | ND | ND | 0.2 |
| 2/27 | 1.8 | 0.4 | 1.1 | 0.2 |
| 2/28 | ND | ND | 0.2 | ND |
| 3/5 | 46 | ND | 0.8 | 0.4 |
| 3/20 | 0.9 | ND | ND | 0.2 |
| 3/27 | ND | 1.0 | 17 | ND |
| 4/2 | ND | ND | 0.1 | ND |
| 4/10 | ND | ND | 0.3 | ND |
| 5/8 | 0.7 | ND | ND | ND |
| 5/22 | 0.6 | ND | ND | ND |
| 6/2 | 0.8 | ND | ND | ND |
| 6/26 | 1.8 | ND | ND | 0.2 |
| 7/10 | 0.9 | ND | ND | ND |
| 7/19 | 1.3 | ND | ND | 0.2 |

---

* Concentration in ug/L.
ND - Not Detected, quantitation limits VOCs = 0.1 ug/L, THM = 0.5 ug/L.
NA - Not Analyzed

In summary, many surface waters may be less protected than ground waters, but the sources and migration of VOC contaminants are easier to identify, follow and control. Surface waters are also generally subject to better cleansing and diluting actions than ground waters.

## Ground Water Characteristics

Ground waters can be subject to natural recharge from rainfall, or surface waters, and contamination from surface and underground waste disposal sites, polluted SW, or surface impoundments. Recharge passes through varying amounts of soil and rock that may provide some biological, chemical or physical removal or transformation of organic pollutants in the recharge water. However, occurrence data (8) and other information (2,3) indicate that significant amounts of VOCs can migrate through the soil and rock, and persist within the water table.

The rate of GW recharge and its effect on the variability in VOC concentrations measured in wells are a complex function of: climate, surface perturbations (irrigation), hydrogeology, type of contaminants carried or dissolved in the recharge water, and pumping effects from nearby wells (9,10). Unlike surface waters, it is often difficult to determine the velocity or direction of flow of ground water, or to identify points of possible contaminant infiltration (9). These uncertainties are reflected in the sampling points and frequencies considered for GWS in Chapters II and V.

Because ground waters tend to move slowly, their quality may vary little with time. Thus, a pristine GW source may remain so for a long period of time; indefinitely if the formation over the aquifer is impervious to contaminants in the soil above it. Some coastal wells of New Jersey are examples of this situation. The spread of VOC contamination in a GW source usually occurs slowly, which allows time to develop treatment technologies or to obtain a new source of water. It also means that a GW source can remain contaminated for a very long time.

The size, slope and other physical conditions of groundwater recharge zones can combine unfavorably with climatic conditions (or varying pumping patterns in the well field) to provide well water of varying quality due to intermittent recharge from contaminated sources. For example, in Bucks County, PA, it was very difficult to determine the extent and source of trichloroethylene (TCE) measured in drinking water wells (10). This was partly because rainfall intermittently diluted the recharge zone, providing well water samples that appeared to be only periodically contaminated with TCE and other VOCs. A similar problem occurred in Endicott, N.Y. where periodic sampling of DW Rainney wells showed varying amounts of VOC contamination. The complete recharge of these wells was rapid, and came from a river into which an upstream discharger was periodically dumping VOCs. This caused large and rapid fluctuations in the well water quality.

Proper control of contamination sources within the cones of influence of all CWS wells is necessary to assess and control the vulnerability of the DW source. To do this, the hydraulic gradients and travel times between contaminated areas and the DW wells are factors that must be determined. Dade County, Fla. has an active and comprehensive aquifer management program that monitors these factors to rate and maintain DW quality (11).

In summary, ground waters are generally more protected and tend to change more slowly than surface waters. However, it is more difficult to remove or reverse an unfavorable trend occurring in a ground water. And it is difficult to assess the vulnerability of GWS to contamination if the geology, recharge conditions and contaminant sources are not known well enough to reliably predict either the possibility of a contaminant infiltrating the source, or the direction or velocity of ground water movement.

### VOC Occurrence Data

In the last ten years, national surveys have been conducted by EPA to measure organic (primarily low molecular weight, purgeable compounds) contamination of drinking waters. There have also been EPA-assisted regional (12) as well as locally-conducted (5,11,13-17) state surveys of drinking water quality. Most of these surveys had significant dissimilarities in design in one or more factors:

1) Process used to select sampling sites,
2) Extent of information about the:
    a) sampling location and conditions
    b) water treatment used
    c) nature of the distribution system
    d) proximity of VOC discharges to the source water
3) Sample collection, shipment and holding procedures,
4) Analytical methodology (especially quantitation limits),
5) Compounds measured, and
6) Inclusion of nonpotable water sources in the occurrence database.

These differences preclude rigorous statistical comparisons between the surveys as well as statistical analysis of the combined occurrence data bases. However, trends in the occurrence data can be used to develop criteria for identifying CWS with water supplies vulnerable to VOC contamination. Some of these trends are summarized below, and the more useful ones are discussed later to support criteria for ranking the vulnerability of CWS.

1) The frequency of occurrence can be both higher, lower or the same in GWS and SWS depending on regional and system size considerations. However, maximum VOC concentrations tend to be significantly higher in GWS than in SWS (18).
2) The frequency and intensity (concentration) increase with the size of the population served by the GWS or SWS sampled (19,20).

3) Proximity of industrial or commercial use of VOCs can be linked to success in locating contaminated CWS; but it is not always a predictor of VOC contaminantion (11,16).

4) A sanitary survey (21) or aquifer protection assessment (11) can sometimes indicate the relative vulnerability of a DW source.

5) The occurrence of even a low concentration of a VOC might indicate substantial contamination of part of the DW source. This is especially true of tap water samples taken in a GW system serviced by varying volumes of water from several wells or well fields that differ in the amount of VOC contamination (22-24).

6) Resample data can show large differences in concentrations and numbers of VOC contaminants. This variability can be caused by factors such as, the difficulty of obtaining a DS sample representative of the source water quality, sporadic VOC dumping activities, pumping rates and rainfall.

No one of these trends, and no single characteristic of ground or surface CWS adequately predicts VOC vulnerability on either a state or national level. But, depending on local conditions and the extent of knowledge of system and water source characteristics, combinations of these factors can help design vulnerabiltiy criteria or scenarios applicable to particular types of CWS. For example, the GWSS nonrandom process used by some state agencies was very effective in locating highly contaminated GWS (20).

Since the highest concentrations of VOCs tend to occur in GWS, most recent monitoring, especially state surveys, has been at GWS. Prior to the late nineteen-seventies GW was generally considered to be pristine and protected.(5) Now, VOC contamination is considered to be a more significant problem in ground waters than in surface waters.

The following overview of selected VOC occurrences is based primarily on GW information. It provides examples of those trends, listed above, that are considered important in developing vulnerability criteria.

The CWS included in five EPA national surveys are categorized below by type of source water used and VOCs measured; "Year" refers to when the major part of the sampling occurred. The number of nine VOCs assayed ranged from two in the NORS to all nine in the GWSS and NSP.

Number of CWS in Five Federal Surveys

| Survey (Year) | GW Sources | SW Sources | # VOCs Assayed |
|---|---|---|---|
| NORS (1975) | 15 | 65 | 2 |
| NOMS (1976) | 19 | 92 | 8 |
| CWSS (1978) | 330 | 106 | 6 |
| NSP (1978-9) | 12 | 106 | 9 |
| GWSS (1981) | 945 | 0 | 9 |

The quality and completeness of these surveys vary. The earliest ones emphasized SWS, and were conducted while sampling techniques, analytical procedures and instrumentation were rapidly changing, and improving in scope and sensitivity.

The CWS participating in three of these surveys have been grouped into three population categories (Table 3); the designations of small, medium and large come from FRDS. Table 4 provides a perspective on the relative number of systems in various population categories, which can be used later to project the cost of the CMR phases. Approximately 80% of U.S. CWS use ground, and 20% use surface, water as a source of supply. Since VOCs may be more of a problem in ground water, it is important to note that 72% (approx. 35,000) of GWS and 3.5% of SWS (approx. 3,900) that serve a combined total of 2.7% of the U. S. populations are very small systems (<500 pop. served).

The NSP set of large surface water systems was picked from a group considered to be more vulnerable than most to organic contamination, whereas the CWSS surface group was more randomly chosen and was biased toward small and medium SWS. The GWSS nonrandom group was more equally divided among the three population ranges than either the GWSS random group or the CWSS GW set. None of these surveys attempted to match the national proportion of CWS in each of the FRDS population categories (Table 4). Not all of the survey interpretations discussed below are based on the FRDS small and medium designations. The CWSS groupings were slightly different (Table 3), and much of the analysis of GWSS data was done on a single division of population-served by the utility being above 10,000

## Table 3

## Population Categories of CWS in Three VOC Surveys

| Survey | System Type | Population Categories* Small | Medium | Large | Total |
|---|---|---|---|---|---|
| CWSS+ | GW | 260 | 41 | 29 | 330 |
| | SW | 53 | 28 | 25 | 106 |
| GWSS | GW random | 244 | 36 | 186 | 466 |
| | GW nonrandom | 204 | 117 | 158 | 479 |
| NSP | GW | 1 | 1 | 10 | 12 |
| | SW | 0 | 1 | 105 | 106 |

---

* Number of systems in each population category:
Small - <3,301 pop.
Medium - 3,301 - 10,000 pop.
Large - >10,000 pop.

+ CWSS only: small category is <2500 pop.; medium is 2,500 - 9,999 pop.

## Table 4

## Characterization of the Water Supply Industry (FY 1982)

| | 65% | | 23% | | | 6.6% | | 4.7% | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Very Small | | Small | | | Medium | | Large | | | |
| Population Served | 25-100 | 101-500 | 501-1000 | 1001-2500 | 2501-3300 | 3301-5000 | 5001-10000 | 10001-25000 | 25001-50000 | 50001-75000 | 75001-100000 |
| Number of Systems | 20,650 | 18,086 | 6,254 | 6,345 | 1,386 | 1,814 | 2,098 | 1,750 | 690 | 219 | 96 |
| Percent of Systems | 34.5 | 30.3 | 10.5 | 10.6 | 2.3 | 3.1 | 3.5 | 2.9 | 1.2 | 0.4 | 0.2 |
| **Principal Source** | 72% | | | 21% | | | | | 7% | | |
| Ground | 19,125 | 15,674 | 4,877 | 4,400 | 891 | 1,065 | 1,168 | 835 | 290 | 64 | 14 |
| Surface | 1,525 | 2,412 | 1,377 | 1,945 | 496 | 749 | 930 | 915 | 400 | 155 | 82 |
| | | | | 69% | | | | | 31% | | |
| **Ownership** | | | | | | | | | | | |
| Public | 1,502 | 7,147 | 4,938 | 5,252 | 1,175 | 1,509 | 1,747 | 1,465 | 502 | 178 | 81 |
| Private | 18,773 | 10,760 | 1,259 | 1,051 | 204 | 302 | 350 | 284 | 188 | 41 | 15 |
| Indian | 375 | 269 | 57 | 42 | 7 | 3 | 1 | 1 | - | - | - |
| **Approximate Population Served** | | | | | | | | | | | |
| (Millions) | 1.19 | 4.51 | 4.64 | 10.34 | 4.02 | 7.46 | 15.17 | 27.87 | 24.92 | 13.39 | 8.32 |
| (Percent) | 0.6 | 2.1 | 2.2 | 4.8 | 1.9 | 3.5 | 7.1 | 13.0 | 11.6 | 6.2 | 3.8 |

---

Source: FRDS07 April 19, 1983

| 0.5% Very Large Over 100000 | Total | |
|---|---|---|
| 272 | 59,660 | |
| 0.5 | 100 | |
| 55 | 48,458 | 81% |
| 217 | 11,202 | 19% |
| 27 | 25,723 | |
| 45 | 33,182 | |
| - | 755 | |
| 32.65 | 214.4 | |
| 43.2 | 100 | |

A-14.a

population (large systems) or below 10,000 population (small and medium systems).

## Federal GW Data

In 1981, EPA measured organic contaminants in 945 drinking water systems (GWSS) using ground water as a source (19). Approximately one-half of the utilities were selected at random; the states selected the other half nonrandomly based largely on expected potential for VOC contamination. An analysis of the results showed general trends based on the size of the population served, and the state's ability to find contaminated sites.

The percentages of supplies in the GWSS containing various concentratrations of VOCs are shown below (19). The occurrence frequencies for one or more of the 26 VOCs measured, were higher in the larger systems than in the smaller systems over all concentration ranges. The 1978 CWSS of 29 large and 301 small† GWS also confirmed this trend: the occurrence frequencies for one or more of 10 VOCs measured in these samples (above the 0.5 ug/L quantitation limit) were 45% and 12% respectively (20).

The occurrence frequencies in the GWSS generally increased with the size of the population group considered, over all concentration ranges regardless of the site selection criterion (random or nonrandom) used. This implies that nearby industrial or commercial or even domestic activity, which presumably correlates positively with population, is a factor in assessing VOC vulnerability.

---

†Defined in Table 3

| GWSS Pop. | Number of Supplies | % of Supplies With Summed Concentrations* of 26 VOCs Greater Than the Value Shown | | | | | |
|---|---|---|---|---|---|---|---|
| | | >QL | >1.0 | >5.0 | >10 | >50 | >100 |
| Random Sample | | | | | | | |
| <3,300 | 244 | 14 | 6.1 | 2.9 | 1.6 | 0 | 0 |
| 3,301 - 10,000 | 36 | 39 | 14 | 2.8 | 2.8 | 2.8 | 0 |
| >10,000 | 186 | 28 | 14 | 6.5 | 3.4 | 0.5 | 0 |
| Nonrandom Sample | | | | | | | |
| <3,300 | 204 | 19 | 8.3 | 2.9 | 2.5 | 0 | 0 |
| 3,301 - 10,000 | 117 | 28 | 21 | 7.7 | 4.3 | 0 | 0 |
| >10,000 | 158 | 37 | 27 | 18 | 14 | 3.8 | 1.9 |

* Concentration in ug/L
QL Quantitation limit (varies for each VOC)

These results also show that the percentage of large systems (37%) contaminated at any concentration greater than the quantitation limit in the nonrandom sample set was about 1.3 times that for the large systems (28%) in the random sample set. This relative proportion of nonrandom to random occurrence frequencies generally increases with increasing concentration. For example, at greater than 10ug/L, the occurrence frequencies for the small, medium and large nonrandomly-selected systems were 1.6, 1.5, and 4.1 times those for the corresponding randomly-selected systems. This indicates that this nonrandom site selection process was useful in locating highly contaminated CWS, especially those serving large populations.

The percent of positive samples in the GWSS nonrandom set is significantly lower than in many state GW surveys. This can be explained by three factors. First, the state data often includes private and nonpotable well monitoring results.

Second, it is biased towards states that have done extensive monitoring, usually as a result of negative information about a GWS; thus, it is not as representative as the GWSS sample set. Finally, although the GWSS nonrandom set was to be selected on the basis of expected contamination, it was not to include previously monitored sites. This excluded sites chosen in the random set of the GWSS, and sites monitored in previous state investigations. States like California, New Jersey, Connecticut, New York and others that had done extensive monitoring of problem areas probably excluded these from their nonrandom choices. In addition, a few states may have chosen new sites that were not necessarily vulnerable; others may have chosen sites based on bacterial rather than organic pollution pollution potential. Thus,the nonrandom study probably did a better job of locating contaminated GWS than this comparison to the random study shows.

The differences in occurrence frequencies between small, medium and large systems, and between randomly and nonrandomly selected CWS are also more pronounced for the nine VOCs considered separately (Table 5). The population trend prevailed over the site selection trend, but again the nonrandom set contained more GWS with high concentrations of the more commonly occurring VOCs (19). These trends also hold for the 9 VOCs considered separately by site selection category (Table 6).

Except for two compounds, the occurrence frequencies in the nonrandom set were greater than in the random set (Table 6), and the differences between these two exceptions are small.

Table 5

9 VOC Occurrences in the GWSS by System Size*

| VOC | Random |  |  |  |  |  | Nonrandom |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Small |  | Medium |  | Large |  | Small |  | Medium |  | Large |  |
|  | % | Med. | % | Med. | % | Med. | % | Med. | % | Med. | % | Med. |
| vinyl chloride | 0 | — | 0 | — | 0.5 | 1.1 | 0 | — | 0 | — | 3.8 | 2.7 |
| 1,1-dichloroethylene | 1.2 | 1.8 | 2.8 | 2.1 | 2.7 | 0.3 | 1.0 | 0.8 | 2.6 | 0.4 | 6.3 | 0.3 |
| 1,2-dichloroethane | 0 | — | 0 | — | 1.6 | 0.6 | 0.5 | 3.4 | 1.7 | 2.6 | 2.5 | 1.8 |
| 1,1,1-trichloroethane | 2.9 | 0.3 | 14 | 0.4 | 8.1 | 1.0 | 5.4 | 0.6 | 12 | 1.2 | 16 | 0.9 |
| carbon tetrachloride | 2.0 | 0.4 | 0 | — | 5.4 | 0.3 | 2.5 | 0.4 | 3.4 | 0.3 | 3.8 | 0.7 |
| trichloroethylene | 2.0 | 0.6 | 11 | 3.5 | 11 | 1.0 | 3.9 | 0.4 | 13 | 1.2 | 24 | 1.5 |
| tetrachloroethylene | 3.3 | 0.4 | 14 | 0.2 | 11 | 0.5 | 6.9 | 0.3 | 11 | 1.3 | 11 | 0.7 |
| benzene | 0 | — | 2.8 | 0.6 | 1.1 | 9.0 | 1.5 | 1.6 | 1.7 | 6.2 | 1.9 | 2.7 |
| p-dichlorobenzene | 0.4 | 0.5 | 2.8 | 0.7 | 1.6 | 0.7 | 1.0 | 0.8 | 1.7 | 0.7 | 0 | — |

---

* - Large System >10,000; Medium 3,301 - 10,000; Small <3,301 pop. served.
% - Occurrence Frequency
Med. - Median of all positive measurements in ug/L.
Random set: 244 small, 36 medium and 186 large systems.
Nonrandom set: 204 small, 117 medium and 158 large systems.

## Table 6

## VOC Occurrence Frequencies in the GWSS and CWSS

| | Ground Water Supply Survey | |
|---|---|---|
| | 466 Random GW Sites | 479 Nonrandom Sites |
| VOC | % | % |
| vinyl chloride (1.0)* | 0.2 | 1.3 |
| 1,1-dichloroethylene (0.2) | 1.9 | 3.1 |
| 1,2-dichloroethane | 0.6 | 1.6 |
| 1,1,1-trichloroethane (0.2) | 5.8 | 10.6 |
| carbon tetrachloride (0.2) | 3.2 | 3.1 |
| trichloroethylene (0.2) | 6.4 | 12.7 |
| tetrachloroethylene (0.2) | 7.3 | 9.4 |
| benzene | 0.6 | 1.7 |
| p-dichlorobenzene | 1.1 | 0.8 |

* Quantitation Limits in ug/L.

† Among the three most frequently occurring VOCs in the GWSS.

small. With a few more exceptions (Table 5), the larger systems in both site categories have higher occurrence frequencies than either of the small system groups. The median concentrations have different trends; with few exceptions the medians for all VOCs, in all population categories, differ by less than a microgram per-liter.

One striking fact from a resample of a GWSS utility was the variability in the finished water quality collected at the WTP (Table 7). Analysis of individual wells in the well field led to the discovery of four contaminated wells. The variability of the WTP water was attributed to pumping patterns that provided varying volumes from each well. This confirms the assertion that contamination of a GW sample warrants searching for the source.

### State GW Data

State monitoring data is summarized in Table 8. It includes results from nonpotable well water samples, and samples collected near hazardous waste storage sites, which accounts for the high occurrence frequencies and maximum concentrations measured. The nonpotable water contamination information may not relate to current consumer exposure, but it can be valuable in predicting the present or future vulnerability of DW sources. Direct comparisons between state surveys are not meaningful, because they represent neither a national, nor always a comprehensive state picture of VOC occurrences in GWS.

The following examples illustrate the variable applicability of trends or vulnerability criteria to specific incidences of VOC contamination.

## Table 7

## Variability of VOCs in Samples* Due to Different Wellfield Pumping Patterns

| Sampling Date | Finished |  | Raw |  |  |
|---|---|---|---|---|---|
|  | c/t | TCE | Well # | c/t | TCE |
| July 8 | 4.3 | 28 |  |  |  |
| Aug. 25 | 77 | 500 |  |  |  |
|  |  |  | 6 | 21 | 330 |
|  |  |  | 17 | ND | ND |
| Oct. 28 | 40 | 450 |  |  |  |
|  |  |  | 6 | 16 | 200 |
|  |  |  | 1 | ND | ND |
|  |  |  | 2 | ND | ND |
|  |  |  | 7 | 83 | 980 |
|  |  |  | 8 | ND | 2.0 |
|  |  |  | 12 | 56 | 220 |

---

* Two VOCs were measured in several samples collected at a GWSS GWS; finished samples collected at WTP, raw samples collected at the well head.

c/t Combined measurement of cis- and trans-dichloroethylene, in ug/L.

TCE trichloroethylene.

ND Not detected, QL is 0.2 ug/L.

# Table 8

## Summary of State Well Water Occurrence Data*

| VOC | # States Tested | % | Max. Conc. (ug/L) |
|---|---|---|---|
| Trichloroethylene | 19 | 15 | 510,000 |
| Carbon tetrachloride | 15 | 14 | 1,300 |
| Tetrachloroethylene | 17 | 17 | 1,000 |
| 1,2-Dichloroethane | 15 | 6.7 | 2,100 |
| 1,1,1-Trichloroethane | 16 | 21 | 2,250 |
| Vinyl chloride | 9 | 7.0 | 380 |
| Benzene | 2 | 0.6 | 17 |

---

* Number of nonpotable or private wells tested is unknown.
% Frequency of occurrence; quantitation limits vary.
Source: EPA VOC RMCL Proposal (Ref. 25).

Michigan phased in a potable well monitoring program by rating the relative vulnerability of their GWS based on: minimal geological protection of the source, suspected improper well construction, or the nearby use of VOCs. The success of these ranking criteria resulted in occurrence frequencies in the first phase that were about twice those for GWS monitored in the second phase of the program (16).

California conducted a public and private well monitoring program for four large groundwater basins. The heavily industrialized San Gabriel Valley had several contaminated wells near the major industrial areas, but no significant contamination was measured in the GWS in the industrialized areas of the Santa Clara ("Silicon") Valley (15).* New York has observed a similar phenomenon, which they explain by stating that the permeability of the formations above the aquifer is better than proximity of VOC use as an indicator of potential contamination (17). Of course, the ubiquity of VOC use, manufacture or disposal throughout New York may also make it easier to apply another vulnerability criterion such as geological protection.

Contamination of several public and private wells, which have been discovered in an ongoing Massachusetts water quality monitoring program, has been attributed to several sources:

---

* However, years later, substantial VOC contamination of urban DW wells was measured, and was attributed to solvent storage tanks. This illustrates that nonoccurrence of a contaminant is not a guarantee that it is not present or nearby.

improper dumping of hazardous wastes into pits, abandoned wells or sewers; underground gasoline tanks, solvent washing operations, Superfund sites, nearby chemical manufacturing, tool industries, machine shops, abandoned landfills, and wool manufacturers (13).

There are many cases where the source of VOC pollution can be neither proven nor predicted. New Jersey has been involved in extensive litigation with suspected polluters; Rockaway Township measured TCE in DW wells despite being in a supposedly pristine and invulnerable area. Pennsylvania had a serious TCE contamination of wells in Bucks County for which several dry cleaners and other light commercial users were thought responsible, but without an extensive and expensive well monitoring program, the exact source(s) and movement of the contamination could not be determined.

Dade County, FL authorities have begun an extensive aquifer management program to assess well water quality, and to control it by regulating surface perturbations and land use (11). Irrigation, land reclamation or development are examples of surface perturbations; waste disposal sites, and industrial or commercial activities are examples of land use. Hydraulic travel times were used in a water quality survey to define wells that were near different types of land use. The results showed that the presence of land development or VOC users did not always lead to large increases of VOCs in nearby wells. But VOC contamination did increase from <0.1 to 57 ug/L, when the volume of VOC use or the extent of land development increased significantly (Table 9).

## Table 9

Average Level of Contamination in Florida Ground Water Samples*

| Prevailaing Land Use, Listed in Ascending Order of Intensity | Volatile Organic Contamination† (ug/L) |
|---|---|
| Undeveloped | 0.0 |
| Residential | 0.1 |
| Residential, canal, industrial | 0.4 |
| Residential, commercial | 0.5 |
| Residential, commercial, industrial | 0.8 |
| Residential | 1.0 |
| Residential, canal, industrial | 1.6 |
| Residential, commercial, industrial | 1.6 |
| Industrial | 2.7 |
| Residential, commercial, canal | 4.6 |
| Industrial, residential | 13.1 |
| Residential, industrial | 20.0 |
| Utility, residential, industrial | 48.7 |
| Industrial, residential | 57.3 |

* Each value represents a different sampling site in the Dade County region of the Biscayne Aquifer.

† Fifteen VOCs that include seven of the 9 VOCs.

Source: Yoder et al., 1981 (Ref. 11).

Some VOCs have occurred unexpectedly in ground water samples collected in Florida. For example, vinyl chloride has been measured in samples where there is no known nearby use, dumping or manufacture. Biological or chemical transformations of other VOCs have been proposed as the origin of vinyl chloride in these samples (4).

The salient point in these and other GW quality studies is that trends can be site specific; no one factor consistently indicates VOC contamination in a GWS. However, a key combination of factors is the use of VOCs near a recharge zone that is permeable to VOCs (17). An analogous situation should hold for unprotected surface waters.

### Surface Water Data

About 20% of the nations' CWS use surface water as their source of supply. The Federal VOC occurrence database for these systems is less complete than the GW database. The same can be said for state data, which tends to emphasize monitoring of ground water systems. The 1976-1977 NOMS was a survey of 92 SWS, most of which were considered to use surface waters subject to persistent VOC discharges. These samples had a higher overall VOC occurrence frequency in unprotected than in protected surface water sources. This result is expected, since unprotected surface watersheds are analogous to geologically vulnerable ground water sources.

While no difference in occurrence frequencies between GWS and SWS (Tables 6 & 10) can be clearly shown, the NSP frequencies and maximum concentrations measured were greater on a compound-by-compound basis than those for the SW set of the CWSS. Since the NSP was biased towards larger and more vulnerable SWS this result is consistent with the expected population and nonrandom trend. Tables 10 & 11 show that higher maximum concentrations of any one VOC tend to occur in GWS rather than SWS.

## Summary

Occurrence data collected in several surveys over the past decade have been examined for trends that indicate a predictable pattern of VOC occurrences. The trends discerned are sometimes contradictory and variable. However, three broad criteria that help predict the relative vulnerability of CWS to VOC contamination are recommended.

These are:

1) the size of the population served by contiguous CWS,
2) the extent of protection of the DW source by natural and regulatory causes, and
3) the nature and extent of VOC use in the area.

## Table 10

## VOC Occurrences in CWSS and NSP Surface Water Systems

| | CWSS | | NSP | |
|---|---|---|---|---|
| Parameter | % | Max. | % | Max. |
| 1,2-dichloroethane | 0 | --- | 0.9 | 4.8 |
| carbon tetrachloride | 2.8 | 2.2 | 14 | 3.0 |
| trichloroethylene | 0 | --- | 6.6 | 3.2 |
| tetrachloroethylene | 2.8 | 3.0 | 6.6 | 3.2 |
| 1,1,1-trichloroethane | 2.8 | 7.0 | 5.7 | 3.3 |
| benzene | 1.0 | 0.6 | 2.0 | 1.8 |
| vinyl chloride | NA | --- | 0.9 | 9.8 |
| 1,1-dichloroethylene | NA | --- | 0.9 | 0.5 |
| p-dichlorobenzene | NA | --- | 0.9 | 0.9 |

CWSS - included 81 small, < 10,000 pop., and 25 large, > 10,000 pop., SWS.
NSP - included 1 small and 105 large SWS.
% - percent occurrence using a common QL of 0.5 ug/L.
Max. - Maximum concentration, in ug/L, measured.
NA - Compound not measured in the CWSS.

## Table 11

## VOC Concentrations* in the GWSS and CWSS

| | GWSS | | CWSS |
|---|---|---|---|
| Chemical | 466 Random | 479 Nonrandom | 330 GWS |
| vinyl chloride | 1.1 | 8.4 | NA |
| 1,1-dichloroethylene | 6.3 | 3.0 | NA |
| 1,2-dichloroethane | 1.0 | 9.8 | 1.8 |
| 1,1,1-trichloroethane | 18 | 21 | 650 |
| carbon tetrachloride | 16 | 15 | 2.8 |
| trichloroethylene | 78 | 130 | 210 |
| tetrachloroethylene | 23 | 69 | 30 |
| benzene | 15 | 12 | 44 |
| p-dichlorobenzene | 1.3 | 0.9 | NA |

---

* Maximum concentration, in ug/L, measured.
NA - Not Analyzed in the CWSS

## Appendix A References

1. Smith, James, et al., ES&T 14, 1332-1337 (1980).

2. Schwarzenbach, R., et al., ES&T 17, 472-479 (1983).

3. Bouwer, E., et al., ES&T 15, 596-599 (1981).

4. Parsons, Frances, et al., JAWWA 76, 2:56-59 (1984).

5. Page, G. William, ES&T 15, 1475-1481 (1981).

6. Manwaring, J.F., et al., Water & Wastes Engineering, pp. 40-45, April 7, 1980.

7. EPA, Feb. 15, 1978, Mar. 27, 1978, May 24, 1978 and Nov. 1, 1978 memoranda from H.J. Brass and R.F. Thomas to Ramon Lee, and a Sept. 20, 1978 memorandum from E.M. Glick to Ramon Lee.

8. EPA, Nine Occurrence Documents for VOCs in DW:

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Benzene, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Dichlorobenzene, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Dichloroethylenes, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Trichloroethylene, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Tetrachloroethylene, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Vinyl Chloride, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, 1,1,1-Trichloroethane, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, August 1983

    EPA, Criteria and Standards Division, Occurrence of Volatile Organic Chemicals in Drinking Water, Carbon tetrachloride, August 1983

9. Ground Water and Wells, Johnson Div., UOP Inc., St. Paul, MN, 1975

10. Witsell, W.J., "Trichloroethylene Contamination of Upper Southampton Well No. 10," EPA, Technical Support Division, Cincinnati, Ohio, June 6, 1980.

11. Yoder, D., et al., ASCE Journal of the Env. Engr. Div., 107 (EEG): 1157-1170 (1981).

12. EPA, "Region VII Survey," TSD Report, Cincinnati, Ohio Jan. 18, 1984.

13. Commonwealth of Massachusetts, Water Quality Issues in Massachusetts, Special Legislative Commission, Boston, MA, Oct. 1981.

14. Tucker, R.K., "Groundwater Quality in New Jersey," DEP Report, March 1981.

15. Nelson, S.J. et al., in Proceedings of ASCE Water Forum, Aug. 10-14, 1981, American Chemical Society of Civil Engineers, New York, N.Y., 1981.

16. Kelley, William E., Memorandum from Michigan Health Department to Dick Reding, July 15, 1983.

17. Marsh, Langdon, "Organic Chemicals in Drinking Water," New York Dept. of Health, Albany, NY, Jan. 1981.

18. EPA, "Occurrence of Volatile SOC in Drinking Water," CSD, December 1981.

19. Westrick, J.J., et al., JAWWA 76, 5:52-59 (1984).

20. EPA, "Final CWSS Data," TSD Report, Cinn., OH, Jan. 30, 1981.

21. EPA, Feasibility Study for a National Comprehensive Water Quality Monitoring Program, EPA Contract 68-03-2909, Athens AERL, Aug. 27, 1981.

22. Gibb, J.P., and M.J. Barcelona, JAWWA 76, 5:48-51 (1984).

23. Scalf, M.R., et al., Manual of Groundwater Quality Sampling Procedures, NTIS #PB82-103045.

24. Keith, S.R., et al., Ground Water Monitoring Review 3, 21-30 (1983).

25. EPA, VOC RMCL Proposal, Fed. Reg. 49 (114), 24330, June 12, 1984.

# APPENDIX B

## Options

### VOCs: Compliance Monitoring and Monitoring for Unregulated VOCs

Provided below are three options for regulations for compliance monitoring and monitoring for unregulated VOCs. These options are summarized in Table B-1.

In each option, requirements are displayed for (1) an initial round of monitoring and (2) repeat monitoring. In addition, different requirements are set within each option for ground water systems (about 45,000) and surface water systems (about 15,000). The primary differences between the options relate to the extent of specific sampling requirements and the provision of State discretion.

### OPTION 1

This option would require all ground and surface water systems to monitor at least once over four years. Relatively stringent federally mandated sampling requirements would be set. Monitoring for unregulated VOCs would be repeated in 10 years.

#### Initial Monitoring

- All systems monitor once over 4 years
- Phase in by size:

| | |
|---|---|
| >10,000 | complete by end of 1 year |
| 3,300-10,000 | complete by end of 2 years |
| <3,300 | complete by end of 4 years |

- Ground water systems:
  - Sample locations
    - Compliance monitoring: sample at each entry point to the distribution system
    - Unregulated VOCs: sample at each entry point to the distribution system

  - Number of samples
    - Compliance monitoring: quarterly sampling for one year (i.e., 4 samples). Require resample of any positive result
    - Unregulated VOCs: one sample and require resample of any positive result

- Surface Water Systems
  - Sample locations: sample in distribution system at points representative of each source.
  - Number of samples: monthly for one year, require resample of any positive results

- Costs for initial monitoring
  - Compliance: $25 million per year for four year (total $100 million)
  - Unregulated: $2.7 million per year for four years (total $10.8 million)

Repeat Monitoring

All systems would be required to remonitor for the nine VOCs on a frequency based upon the results of the first monitoring and their vulnerability to VOC contamination. All systems would be required to repeat the monitoring for unregulated VOCs in 10 years (for unregulated VOCs that were detected in the initial monitoring it would be anticipated that States would require follow-up investigative monitoring).

| • **Status*** | **Frequency** |
|---|---|
| Compliance Monitoring: | |
| VOCs not detected and invulnerable | Repeat in 5 years |
| VOCs not detected and vulnerable | Repeat in 3 years |
| VOCs detected | Monthly |
| Monitoring for unregulated: | Repeat in 10 years |

*States would recertify annually vulnerability status.

- Costs for repeat monitoring
  - Compliance monitoring: $64 million/year
  - Unregulated monitoring: $2.7 million/year

## OPTION 2

This option would require all ground and surface water systems to monitor at least once over four years. Fewer samples would be required during the first round of monitoring than in Option 1. Ground water systems would be required to repeat compliance monitoring at a frequency based upon vulnerability and monitoring results. Repeat monitoring by surface water systems would be at State discretion. No repeat monitoring for unregulated VOCs would be federally mandated.

### Initial Monitoring

- All systems monitor once over 4 years
- Phase in by size:

| | |
|---|---|
| >10,000 | complete by end of 1 year |
| 3,300-10,000 | complete by end of 2 years |
| <3,300 | complete by end of 4 years |

- Ground water systems:
  - Sample locations
    - Compliance monitoring: sample at each entry point to the distribution system
    - Unregulated VOCs: sample at each entry point to the distribution system
  - Number of samples
    - Compliance monitoring: quarterly sampling for one year; if first sample detects no VOCs, State can reduce monitoring to that one sample. State discretion on confirmation sample
    - Unregulated VOCs: one sample; State discretion on confirmation sample

- Surface Water System

| | |
|---|---|
| - Sample locations: | sample in distribution system at points representative of each source |
| - Number of samples: | quarterly for one year; State discretion on confirmation samples |

- Costs for initial monitoring

| | |
|---|---|
| - Compliance: | $9.3 million per year over four years (total $37 million) |
| - Unregulated: | $2.3 million per year over four years (total $8 million) |

Repeat Monitoring

Repeat compliance monitoring would be based upon vulnerability and if VOCs were detected, similar to Option 1. Repeat compliance monitoring for surface water systems would be at State discretion. Repeat monitoring for unregulated VOCs would be at State discretion.

| • Status* | Frequency |
|---|---|
| Compliance Monitoring: | |
| VOCs not detected and invulnerable | Repeat in 5 years |
| VOCs not detected and vulnerable | Repeat in 3 years |
| VOCs detected | Monthly |
| Monitoring for unregulated: | State discretion |

*States would recertify annually vulnerability status.

- Costs for repeat monitoring:

| | |
|---|---|
| - Compliance: | $17 million per year |
| - Unregulated: | $0 |

OPTION 3

This option would require all ground water systems to monitor at least once over five years. Monitoring of surface waters would be at State discretion based upon vulnerability.

Monitoring for unregulated VOCs would only require samples representing 25% of the wells in each ground water system. State discretion would be provided for repeat sampling frequencies for systems not detecting VOCs in the first round. No repeat monitoring would be required for unregulated VOCs.

Initial Monitoring

- All systems monitor once over 5 years
- Phase in by size:

| | |
|---|---|
| >10,000 | complete by end of 1 year |
| 3,300-10,000 | complete by end of 2 years |
| 500-3,300 | complete by end of 4 years |
| <500 | complete by end of 5 years |

- Ground water systems:
  - Sample locations
    - Compliance monitoring: sample at each entry point to the distribution system
    - Unregulated VOCs: sample at each entry point to the distribution system
  - Number of samples
    - Compliance monitoring: one sample; State discretion on confirmation sample
    - Unregulated VOCs: number representing 25% of wells in each system. State discretion on confirmation sample
- Surface Water Systems: State discretion based upon vulnerability assessment
- Costs for initial monitoring
  - Compliance: \$3.8 million over 5 years (total \$20 million)
  - Unregulated: \$0.5 million over 5 years (total \$1.5 million)

## Repeat Monitoring

Repeat compliance monitoring would only be for those systems that detected VOCs in the first round. Other systems would be at State discretion. No federally required repeat monitoring for unregulated VOCs.

| • Status* | Frequency |
|---|---|
| VOCs not detected and invulnerable | State discretion |
| VOCs not detected and vulnerable | State discretion |
| VOCs detected | Annually |
| Monitoring for unregulated: | State discretion |

*States recertify annually vulnerability status.

- Costs for repeat monitoring:
  - Compliance: $2.9 million per year
  - Unregulated: $0

## Other Factors for Reduction in Monitoring

- Require sampling for vinyl chloride only in ground water systems that had detected other chlorinated 2-carbon VOCs.
- Systems with recent valid monitoring data would not be required to conduct the monitoring; i.e., "grandfather" waiver. Minimum QA requirements would have to be met.
- States could reduce monitoring for ground and surface water systems that detected VOCs below the MCL after a baseline period of data are generated.
- States would reduce monitoring for systems that took a well out of service that had detectable levels of VOCs.

## TABLE B-1

### Summary: Monitoring Options

| | Option 1 | Option 2 | Option 3 |
|---|---|---|---|
| **Initial Round** | | | |
| Time to Complete | 4 years | 4 years | 5 years |
| Ground Water Systems: | | | |
| Compliance* | Quarterly: 4 samples/ confirmation | Quarterly: State can reduce to 1 sample | 1 sample |
| Unregulated | 1 sample/ confirmation | 1 sample | 1 sample at 25% of wells |
| Surface Water Systems: | | | |
| Compliance and Unregulated | Monthly for one year | Quarterly for one year | State Discretion |
| Costs | | | |
| Compliance | $25 million per year | $9.3 million per year | $3.8 million per year |
| Unregulated | $2.7 million per year | $2.3 million per year | $0.5 million per year |
| **Repeat Monitoring** | | | |
| Compliance* | | | |
| VOCs ND/Invulnerable | 5 years | 5 years | State Discretion |
| VOCs ND/Vulnerable | 3 years | 3 years | State Discretion |
| VOCs detected | Monthly | Quarterly | Annually (Ground Water Systems)<br>State Discretion (Surface Water Systems) |
| Unregulated | 10 years | None | None |
| Costs | | | |
| Compliance | $64 million per year | $17 million per year | $2.9 |
| Unregulated | $2.7 million per year | $0 | $0 |

*Vinyl chloride would only be required for systems that had detected other chlorinated 2-carbon VOCs. No requirements for vinyl chloride in surface water systems.

# APPENDIX C

## Method Detection Limits (MDLs) and Practical Quantitation Levels (PQLs)

EPA defines the method detection limit (MDL) as the minimum concentration of a substance that can be measured and reported with 99% confidence that the true value is greater than zero. The specification of such a concentration is limited by the fact that detection limits are a variable affected by the performance of the entire measurement system. MDLs are not necessarily reproducible over time in a given laboratory even when the same analytical procedures, instrumentation and sample matrix are used.

The level that can be achieved reliably within reasonable limits of precision and accuracy by laboratories analyzing compliance samples will be defined here as the Practical Quantitation Level (PQL). The PQLs for VOCs have been determined from theoretical concepts, practical experience and from data gathered from performance evaluation studies.

Available performance data summarized in Table 4 of this report (Chapter 4; page 40) indicates that many laboratories can perform acceptably using ± 40% acceptance limits at concentration levels around 5 ug/L. Presently, performance data are not available at concentration levels of 1 ug/L. Further, performance data are not available for 1,1-dichloroethylene and vinyl chloride at any concentration level. In cases where performance data are not available to determine the PQL, theoretical and practical considerations can be used to estimate the PQL.

Glaser et.al. (1) have recommended that "If the level of analyte in the sample is below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, no measured value is reported." This statement suggests that the uncertainty of a measured value is greater at concentrations approaching the determined MDL. Their recommendation concerning "10 times the MDL" was made based on practical experience with the wastewater methods. Since drinking water samples tend to be "cleaner" samples, a somewhat lower factor may be reasonable for reporting a measured value.

These authors also discuss confidence interval estimates for the calculated MDL. The 95% confidence limits for the MDL result in the following expressions:

$$LCL_{MDL}=0.64\ MDL$$

$$UCL_{MDL}=2.20\ MDL$$

where $LCL_{MDL}$ and $UCL_{MDL}$ are the lower and upper 95% confidence limits of the MDL based upon the determination of MDL by analyzing seven aliquots. Thus, from a theoretical standpoint, a measured value should not be reported in any case if it is less than 2.2 times the MDL.

Taking into consideration the concepts discussed by Glaser et al., it is reasonable to set the PQLs for VOCs in a range between 5 to 10 times the MDL. With MDLs in the range of 0.2 to 0.5 ug/L for these VOCs, the resulting PQLs for VOCs would fall in the 1 to 5 ug/L range.

Vinyl chloride poses a greater analytical challenge than the other VOCs because of the nature of the standards and the calibration procedure used in the analysis. In view of the special attention needed during analysis and the observation that vinyl chloride consistently occurs in ground waters in the presence of other halogenated two-carbon VOCs, monitoring for vinyl chloride will be exempted for ground water systems when the systems demonstrate the absence of two-carbon VOCs. Analysis of six specific VOCs will be required as a condition of this monitoring regime.

Due to the fact that a much smaller number of systems would be required to monitor for vinyl chloride as opposed to other VOCs, the more conservative approach in setting the PQL for vinyl chloride is being proposed. The determination of the proposed PQL for vinyl chloride has been made by taking the low end of the detection limit range given earlier (0.2 ug/L) and multiplying by a factor of 5, resulting in an PQL of 1 ug/L for this contaminant. For the other VOCs, the PQL has been proposed at 5 ug/L since this level should be achievable by a larger number of State and commercial laboratories performing compliance VOC measurements on a routine basis.

## Appendix C Reference

1. Glaser, J.A., *et al.*, Env. Sci. and Tech., Vol. 15, No. 12, pp. 1426-1435.